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PHYSICAL REVIEW.

THE EVOLUTION OF HYDROGEN FROM THE CATHODE AND ITS ABSORPTION BY THE ANODE IN GASES.[1]

By Clarence A. Skinner.

WHILE making an experimental study of the cathode fall of various metals in helium it was observed that no matter how carefully the gas was purified the hydrogen radiation, tested spectroscopically, persistently appeared in the cathode glow. Simultaneous with this appearance there was also a continuous increase in the gas pressure with time of discharge. This change in gas pressure was remarkable because of its being much greater than that which had been observed under the same conditions with either nitrogen, oxygen, or hydrogen.

Now the variation in the cathode fall with current density and with gas pressure in helium was found to be so like that obtained earlier with hydrogen[2] that it appeared necessary to maintain the helium free of the latter in order to make sure that the hydrogen present was not the factor causing this similarity in the results. Futile endeavors to attain this condition led to the present investigation, which locates the *source of the hydrogen in the cathode*, shows that *the quantity of hydrogen evolved* by a fresh cathode *obeys Faraday's law* for electrolytes, and that a fresh *anode absorbs hydrogen according to the same law.*

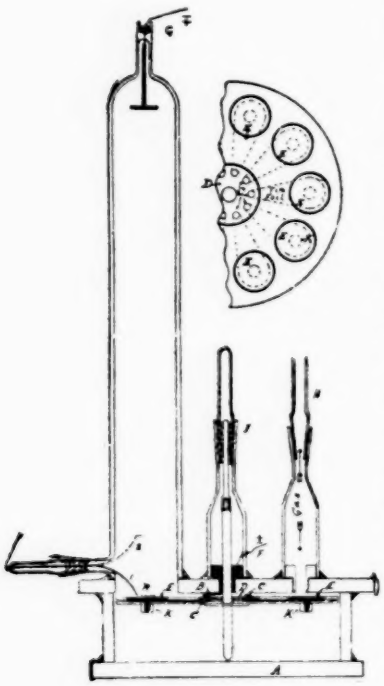
[1] Read in part before the Am. Phys. Soc. at Philadelphia, December, 1904.

[2] Phil. Mag., September, 1904.

PREPARATION AND APPARATUS.

Helium was obtained by heating dry clevite. The gases thus generated stood for some time in tubes containing respectively crushed potassium hydrate and phosphorus pentoxide. From these it was passed into a final purifying chamber consisting of a discharge tube possessing for a cathode an alloy of sodium and potassium, which according to Mey[1] absorbs nitrogen, oxygen, and hydrogen leaving only argon as an impurity in the helium. From this chamber the gas was passed at will into the regular discharge tube containing as electrodes the metals to be tested.

Fig. 1 represents a vertical section of this discharge tube ending below in a larger cylindrical chamber (axis vertical), the whole of glass construction. Ten electrodes E (circular disks 15 mm. in diameter) were attached to the face of a circular glass plate at equal intervals by hard rubber caps K (see also plan in Fig. 2). This glass plate, mounted in the cylindrical chamber, could be rotated about its axis by the key introduced through the ground joint J, and by this means any electrode brought into position at the lower end of the discharge-tube. A hard-rubber disk D, studded with brass rivets C and fixed to the circular plate, served to complete the electric circuit from F through the metal collar and attached spring-brush B to the tinfoil strip leading to its corresponding electrode E. By this device all electrodes, with the exception of the one in use, were isolated from the circuit. To confine the discharge solely to the face of the electrode, a second circular glass plate properly cut



Figs. 1 and 2.

[1] K. Mey, Ann. d. Physik (4) 11, p. 127.

was pressed closely on top of the first, covering the tinfoil strips and fitting the rim of the electrodes. Leakage from the brush *B* to the gas was avoided by reducing the space between the upper face of the electrode-plate and the roof of the chamber to about .5 mm. thickness. The discharge-tube was 3 cm. in diameter and about 20 cm. long. All permanent joints of this apparatus which could not be fused were cemented first with water-glass (sodium silicate), then, in addition, they were covered on the outside with de Khotinsky's laboratory cement. The base-plate *A*, which had to be removed to allow for repolishing the electrodes, was sealed by simply applying the latter cement on the outside of the juncture, care being taken that it did not extend to the inner part. This tube proved to be in all cases absolutely airtight.

In connection with this discharge-tube which will be designated as the electrode-tube, was a second Na,K purifying chamber which usually remained in open connection with the electrode-tube so that impurities in the gas filling could be absorbed by simply passing a current from the Na,K as cathode. This allowed also a careful test to be made for any absorption of helium during the operations.

Customary precautions against the presence of moisture were taken. The system on first evacuation remained open to P_2O_5 as dryer at least twenty-four hours, but after that time during all qnantitative tests the drying chamber was cut off by a stop cock. Any moisture appearing, however, would have been wholly removed by the purifying discharge.

Stop cocks and ground joints were lubricated with a mixture of vaseline, rubber and paraffine recommended by Travers[1] as being free of hydrocarbons.

A McLeod gauge served to measure the gas pressure, magnifying it one hundred times.

The electric current was furnished by a battery of small accumulators and measured by a Weston milliammeter.

Hydrogen is Evolved Solely from the Cathode.

Out of various experiments the following are given as representative of the results obtained.

[1] The Experimental Study of Gases.

Helium was prepared and purified and described above. A spectroscopic observation of the discharge in the first Na,K chamber revealed only the lines of helium and argon.

Electrodes of ten different metals having been polished and mounted in the electrode-tube, this with the second Na,K tube and connected chambers was evacuated and left over night open to the P_2O_5 drying chamber. The evacuation was carried the next day to about one thousandth of a millimeter after which the drying chamber with pump was cut off from the rest of the system.

Helium was then admitted to the electrode tube and connecting chambers at a pressure of about three millimeters of mercury. In order to remove the last trace of foreign gases a discharge was passed for some time through the second Na,K tube. The pressure of the gas under this discharge remained unchanged, showing that the spectroscopic test made in the first Na,K tube was reliable.

An electric current of 2 ma. was now passed from one of the electrodos E (Figs. 1 and 2) as cathode and immediately the spectrum of hydrogen appeared in the cathode glow.[1] The gas pressure also increased continuously with the time the current was maintained. After running about three quarters of an hour the rate of evolution of gas became very small. This extra gas evolved (for silver about .2 c.c. at atmospheric pressure) could be absorbed by the Na,K discharge in about an hour.[2] If at the end of this time a current was passed through the tube as before the gas pressure began to increase as at first, but dropped within a very short time to a low rate of evolution. If now at this point a new metal were used as cathode there took place as usual a continuous increase in gas pressure — the rate of evolution of gas being the same for all fresh cathodes. This experiment repeated at various times and with different metals showed beyond doubt that the source of gas was solely in the cathode.

Sixteen different kinds of metals have been tested as cathodes

[1] No trace of the hydrogen spectrum appears at any other part of the discharge. The helium radiation itself is obliterated by the argon in the positive column. See Nutting, Bureau of Standards Bulletin, Vol. 1, No. 1.

[2] It was always observed that under this purifying discharge the gas pressure returned to, but never went below, its original value — this showing very definitely that helium did not disappear from the gas filling during any of the operations.

and all except two found to give off hydrogen at a measurable rate. The exceptions were the Na,K alloy which as cathode absorbs hydrogen, and mercury which was distilled in vacuo, then tested without having been in the meantime exposed to the atmosphere.

While studying previously the electrode fall in nitrogen, oxygen and hydrogen the gas pressure was found to change very differently with the different gases. Nitrogen increases slowly with the time the current has been passing; oxygen, open to a drying chamber, decreases at a marked rate; while hydrogen was seldom found to change appreciably, though there were occasions where a slight increase was recorded even with hydrogen. If now hydrogen is liberated from the cathode in all gases we should expect in nitrogen an increase in gas pressure arising from the formation of ammonia, which takes place when a discharge passes through a mixture of nitrogen and hydrogen. In this case the rate of increase in gas pressure, compared with that in helium, is small since six atoms of hydrogen would be required to change one molecule of nitrogen into two molecules of ammonia, while in chemically inactive helium one new molecule of gas is formed from two atoms of hydrogen. Likewise with oxygen water vapor would be formed and absorbed by the dryer, in which case four atoms of hydrogen would cause a decrease of one molecule in the gas filling. Of vital interest therefore must be the fact that in hydrogen there is practically no change in the gas pressure when a current passes through it. Experiments described below indicate that in this case the anode absorbs at the same rate as the cathode evolves the hydrogen. Hence we conclude that in all gases hydrogen is evolved from the cathode.

It is rather remarkable that other gases are not present to an appreciable extent. Only in a few cases and that on first usage after polishing has a trace of nitrogen also been observed. Aluminium and tin were noted as giving off a trace of nitrogen.

The Metal Recovers a Supply of Hydrogen by Diffusion from Within.

An endeavor was made to deplete the metals of their supply of hydrogen by passing from them as cathode a current for a sufficient

length of time, but it was soon found that they recovered more or less rapidly from their apparently depleted condition. Silver which exhibits this property of recovery to a high degree happened to be the first metal tried and it was so persistent in regaining its original store that other metals have received comparatively slight attention though all have been observed to possess within themselves the property of recovering to a certain degree their ability to give off hydrogen.

With a freshly polished metal as cathode the gas pressure increases at first at a constant rate, but after a time this rate begins to drop off until the pressure appears to have reached a constant maximum value. Silver was depleted in this way giving off about two tenths of a cubic centimeter (measured at atmospheric pressure) of hydrogen. The current was then broken and the hydrogen absorbed by the Na,K cathode. After standing in the helium over night then tested again the next morning it was found to have a new supply equal to the one given up the day before. Without allowing it any chance of regaining hydrogen from an external source it was thus depleted six or eight times during the course of two weeks and found to give off at each time about the same amount of gas. With an hour's rest only a slight recovery was noticed.[1]

After this series the silver was removed from the tube, repolished, then tested again with the same results. Altogether about two cubic centimeters of gas have been given off by this silver disk, which is 15 mm. in diameter and about one millimeter thick. It shows no sign of having its supply of hydrogen reduced in the least. There are other metals of which cadmium is an example which seem to possess more of a surface charge of hydrogen. This metal, however, seems to reach an apparently depleted condition before the hydrogen it really possesses (measured by vaporizing the surface) is half gone.[2]

[1] H. A. Wilson has observed a similar recovery in case of the escape of negative electricity from hot platinum. Phil. Trans., 202, p. 243, 1903.

[2] A single experiment was performed in which the surface of a cadmium cathode was vaporized by an extra large current. The cathode gave off about one third of a cubic centimeter of gas with the first vaporization. With a second an inappreciable quantity was freed as if its supply had been exhausted.

Just what takes place, therefore, causing the metal to appear depleted is not clear. Undoubtedly the tarnish which appears on the surface of all metals as cathode plays a part in decreasing the diffusion of hydrogen outward from metal into gas. It is natural to suppose that with this present, the hydrogen after discharging to the positive gas ion which has penetrated this film, diffuses more readily back into the metal than outward through the film. Thus it has been noted that those metals, like silver, which tend to keep clean by the process of dusting off onto surrounding bodies will completely recover with rest, while aluminium for example, which under first usage gives off hydrogen with remarkable freedom, but which does not dust off appreciably, recovers but slightly after its surface becomes once tarnished.

All metals are renewed by being repolished, but whether this arises wholly from cleaning the surface of the metal or partly also from exposure to the moist atmosphere remains undecided. The kind of polish used does not seem to affect the results.

This question of depletion is considered again in connection with the experiments on steel cathodes differing greatly in discharge area.

Tested at Low Pressures the Metals do not Absorb Hydrogen in the Molecular State.

It is of first importance to know under what conditions the metals gain their store of hydrogen. The metallurgical processes may account for it in many cases but it is questionable if all metals would retain the gas to such a concentration through the processes of fusion to which they are subjected.

Platinum is a well-known representative of metals which, with evolution of heat, absorb hydrogen in large quantities — giving it up again as the temperature is raised. Now it may be possible that the other metals also absorb hydrogen in relatively smaller quantities. The apparatus as it stood allowed a delicate test to be made at low gas pressures. Hydrogen was driven out of the different metals in the electrode tube to a pressure of about one half millimeter in three millimeters of helium. This was left standing in the tube over night. The next day the gas pressure was found unchanged. The quantity of hydrogen reabsorbed by the metals was less than one twentieth part of the amount the silver alone recovered

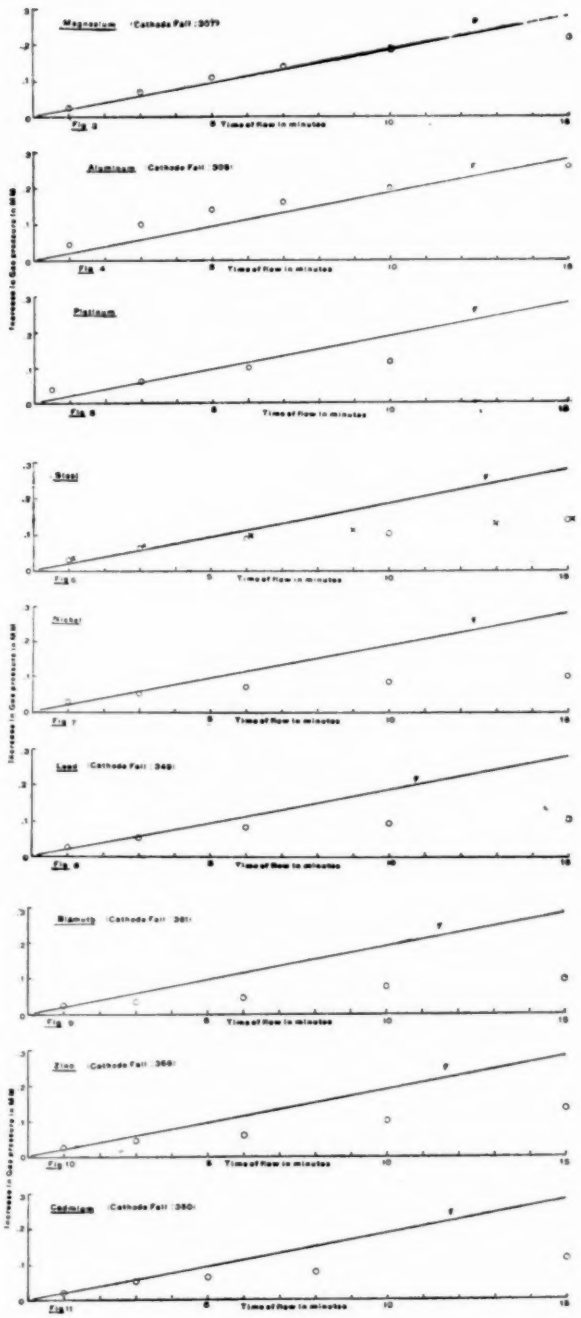
in that time. This experiment shows that the hydrogen in the molecular state is not at such low pressures absorbed by the metals. It is, however, by no means conclusive, for, from a thermodynamic standpoint we should expect absorption to take place with the pressure sufficiently great.

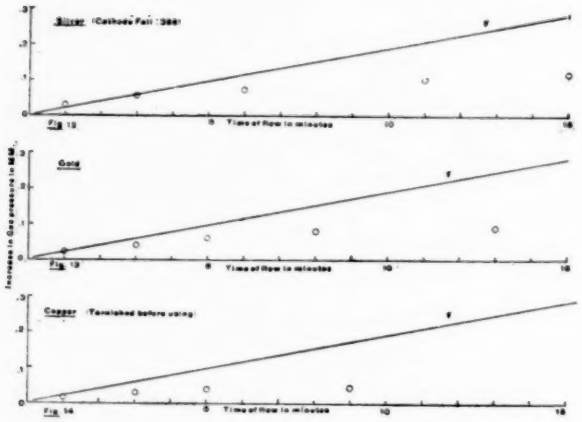
The indications are that in the metal the hydrogen exists in the atomic state rather than in the molecular. It is probable, therefore, that hydrogen in the atomic state would be readily absorbed by the metals while no appreciable amount is taken up if the gas be in the molecular state. Some metals, such as platinum and palladium, appear able to dissociate and absorb large quantities of hydrogen. Any dissociating agent such as water might, therefore, render hydrogen in a form readily absorbed by all metals.

THE QUANTITY OF HYDROGEN EVOLVED FROM THE CATHODE OBEYS FARADAY'S LAW.

Measurements were made of the rate of evolution of hydrogen from cathodes of various metals. This was obtained by first determining the space occupied by the gas (620 c.c.) and then from the increase in gas pressure calculating the quantity of hydrogen given off. Ten electrodes could be tested without opening the tube or even changing the gas filling. The metals were freshly polished and introduced into the tube which was immediately evacuated and left standing open to the drying chamber over night. The next day after continued evacuation the drying chamber and pump were cut off and helium admitted at the desired pressure. Before passing a current through the electrode tube a purifying discharge was passed through the Na,K tube to assure the removal of any trace of foreign gases. After testing one metal the gas evolved was absorbed by the purifying discharge, then another metal immediately tested. With the exception, therefore, of the lapse of time all metals were tested under identical conditions.

Results with a current of 2 ma. in helium at 3 mm. pressure are represented by points in Figs. 3–14, in which the ordinate of each point represents the increase in gas pressure while the corresponding abscissa represents the time the current had been flowing. The diagonal line F in each figure shows the calculated increase in gas


Magnesium (Cathode Fall : 307)
Fig. 3
Time of flow in minutes
Aluminium (Cathode Fall : 309)
Fig. 4
Time of flow in minutes
Increase in Gas pressure in MM
Platinum
Fig. 5
Time of flow in minutes
Steel
Fig. 6
Time of flow in minutes
Nickel
Fig. 7
Time of flow in minutes
Increase in Gas pressure in MM
Lead (Cathode Fall : 349)
Fig. 8
Time of flow in minutes
Bismuth (Cathode Fall : 361)
Fig. 9
Time of flow in minutes
Zinc (Cathode Fall : 366)
Fig. 10
Time of flow in minutes
Increase in Gas pressure in MM
Cadmium (Cathode Fall : 380)
Fig. 11
Time of flow in minutes



pressure if Faraday's law for electrolytes should govern the evolution. All metals show that the hydrogen is liberated for a time at a rate sufficient to carry, as negatively charged atoms, the whole current between cathode and gas. After a lapse of time, varying in magnitude with the kind of metal used, the rate of evolution drops below that required by Faraday's law. The tendency is general for the metals to give off in the first minute a quantity greater than that necessary. This extra pressure does not arise from heating nor from dissociation of the gas under the current, for these effects were found too small to be observable. It is probable that the current on "making" the circuit is extra large, but of such short duration as not to be revealed by the ammeter. Experiments with hydrogen described below show that it cannot arise from *neutral* gases freed from the electrode and chamber walls.

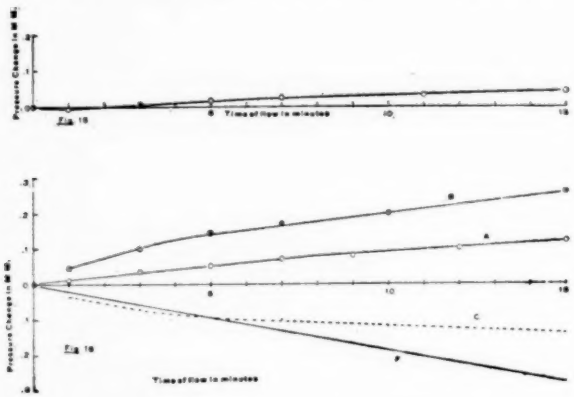
Other tests made with helium, down to a pressure of one millimeter, and also with currents varying from one to three milliamperes corroborated this law, though experimental conditions were not so favorable for making reliable measurements. For with larger currents pressure observations could not be read rapidly enough, and at lower gas pressures the Na,K cathode does not absorb the last trace of hydrogen so that the assurance was lacking that a disturbing quantity of hydrogen was not already present. The experiments were extended, however, to test the effect of a greatly varied current density at the cathode. The current density in the experiments de-

scribed above was about six times the normal, or minimum, value for helium at that pressure. Another experiment was performed using a steel wire (diam. 3 mm.) as cathode. With a current of 2 ma. and pressure of helium 3 mm. the normal discharge area was 10 sq. cm. The pressure change with this cathode is given by the crosses in Fig. 6; while that observed with a steel disk (discharge area, 1.7 sq. cm.) is represented by circles. The two sets of results are practically identical over the whole range. Evidently the deviation from Faraday's law, being the same with both cathodes, cannot be ascribed simply to exhaustion of the store of hydrogen, for in that case the wire should have kept up about six times as long as the disk. If, on the other hand, it be ascribed to tarnish alone, this must take place at a rate which is the same for greatly different current densities. Another possible factor is the absorption of hydrogen by the anode, but since the quantity here makes up less than one per cent. of the gas filling anode absorption could not be expected to play an appreciable part. The difference in results from the different metals also precludes this as a possible explanation.

A comparison of the length of time the different metals follow Faraday's law in furnishing hydrogen brings to light an interesting relation between this and their cathode fall when fresh. It is a well-known fact that aluminium and magnesium possess in all gases a lower cathode fall than the rest of the more electronegative metals. In several of the foregoing figures is given the cathode fall (obtained during another series of experiments) of the fresh metal in helium under a current of 0.6 ma. and gas pressure of 2 mm. With the difference in cathode fall aluminium and magnesium are to be distinguished from the other metals in a more striking manner by the freedom with which they continue to give off hydrogen. These results suggest that there must be an intimate connection between the cathode fall of the fresh metal and the length of time the metal holds up in furnishing hydrogen. Though the quantity of hydrogen possessed by such metals as platinum and silver is much greater than that possessed by aluminium and magnesium, we find the latter give off during a fifteen-minute run about twice as much as the former, indicating that the cathode fall must be affected to no small extent by the rate with which the hydrogen diffuses through the metal.

IN HYDROGEN THE ANODE ABSORBS AT THE SAME RATE THE CATHODE EVOLVES IT.

Reference has already been made to the fact that earlier observations with a hydrogen filling show only occasionally a slight increase in gas pressure. Thinking it probable that we have in this case to do with absorption by the anode neutralizing the evolution from the cathode a test was made to see what takes place under a longer run than was made in earlier experiments. With the silver disk as anode and an aluminium wire, of about half the discharge area of the silver, as cathode, a current (2 m.a.) was passed through hydrogen at pressure 3.45 mm. and pressure measure-



ments made at definite intervals. The observed change is represented by the curve in Fig. 15. During the first three minutes of discharge the gas pressure remained practically unchanged, but at the end of that time it began to increase at a measurable rate. The most natural explanation of these results seems to be that of anode absorption. At first the anode absorbs all negative atoms discharging to it. These do not diffuse into the metal as rapidly as they are given off by the cathode, therefore the concentration in the anode surface increases up to a point where uncharged atoms diffuse out again into the gas. Beyond this point the curve would therefore represent the difference between the rate of diffusion out of the cathode and that into the anode.

If this be the correct explanation the effect should be magnified by taking an anode of much smaller discharge area than the cathode

possesses. This experiment was tried. The cathode was the disk of aluminium used in the experiments described above. For anode an aluminium wire sheathed with glass tubing was used giving a discharge area something less than one tenth that of the cathode. Observations were made in hydrogen as before (current 2 ma., gas pressure 3 mm.). The results given in Fig. 16, curve *A*, substantiate the supposition just expressed. The pressure begins to increase before the discharge has continued one minute. The form of the curve is that which might be expected as a difference between cathode evolution and anode absorption. Assuming that the cathode gives off hydrogen at the same rate here as in helium (represented by curve *B*) the curve *C*, representing anode absorption is obtained as the difference between the *A* and *B* curves, the anode absorption tending to reduce the gas pressure by the amount indicated. The general form of this curve appears to be the same as that given by cathode evolution in helium. Here the line *F* represents absorption demanded by Faraday's law. These experiments indicate therefore that *in hydrogen a fresh anode absorbs gas at a rate also determined by Faraday's law.*

Discussion.

Some interesting conclusions, drawn from the experimental results recounted on the preceding pages, may be stated briefly.

With fresh electrodes the hydrogen atom serves in all gases as carrier of the electric current from cathode to gas. With a gas filling of hydrogen the atom serves also as carrier from the gas to the anode — by which it is absorbed. In helium on the other hand the hydrogen atom leaving the cathode discharges to the helium and this transmits the current to the anode, the negative helium ion discharging without being absorbed.

Most remarkable of all is the fact that, though there is a considerable concentration of *free positive ions* at the cathode surface, *they do not discharge to the metal* so long as it furnishes hydrogen sufficient to carry the current. This condition may last several minutes. Even the positive hydrogen ion does not enter into electrical union with the metal, though a negatively charged hydrogen atom is readily absorbed by it.

The generally accepted view that the negative ion in gases is of smaller magnitude than an atom while the positive ion is of molecular (or atomic) magnitude evidently does not hold there. We have strong evidence in the above experiments that in hydrogen a hydrogen atom carries the current from cathode to the gas, then again from the gas to the anode. This being true any other form of ionization in the gas between cannot be expected. If now this occur with hydrogen we should expect no other than atomic ions under the same conditions in other gases. Conduction in other gases would however be modified by the fact that the negative hydrogen atom freed from the cathode serves as the active ionizing agent. This fulfills in all gases except hydrogen the requirement that the negative ion be much smaller than the positive ions it produces. Of special interest in this connection are the results recently published by Townsend.[1] He finds that the positive hydrogen ion possesses an unexpectedly large ionizing power, which seems to agree with the views just presented requiring that the only difference between the ionizing power of the negative ions freed from metals (negative hydrogen atoms) and positive ions produced in hydrogen (positive hydrogen atoms) be that arising from the difference in sign of the charge carried.

The effect of an electric current and radiations in producing chemical combination of gas mixtures receives on this basis a simple explanation. The gas molecules are broken up into their constituent atoms and these recombine, forming the new compound.

Some light also is thrown by these experiments on the problem as to why positive gas ions do not discharge to a negative metal but instead draw out of the metal the negative hydrogen ions. It appears that an intimate association in the atomic form is necessary to a transmission of charge from gas to metal. Now hydrogen in acids is universally the carrier of positive electricity. In solutions of metallic salts the metals carry universally the positive charge. Here, however, when we have an electrical union of hydrogen with the metals, the hydrogen becomes the carrier of the negative charge. The natural union therefore of all gases with metals should be that where the metallic atom is positively charged and the gaseous atom

[1] Phil. Mag., December, 1904.

negatively charged. If this be reversed — the metal being charged with negative electricity and the gas with positive — a union only takes place under very great external forces. For as the cathode becomes depleted the electric force at the boundary between it and the gas is increased greatly. This conclusion is derived from observations made on the cathode fall in nitrogen. About three years ago[1] the writer observed with a steel cathode in nitrogen that there was at first, as usually observed, a strong electric field out in the gas between the cathode and the inner boundary of the negative glow. After, however, a sufficiently large current was passed for a few moments this field dropped to practically zero. At the same time, however, the fall of potential between the cathode and the negative glow increased, which shows that there must have taken place a considerable increase in the electric force at the boundary between metal and gas. This change is now recognized as that where the hydrogen ceased to be furnished by the cathode as required by Faraday's law. It may be possible that this represents the force required to cause the positive ions of the gas to discharge to the metal at the rate demanded by the current. It may be that such an electrical union is wholly impossible, and cathode rays a result. A most interesting experiment in this connection would be one to determine what effect, if any, the hydrogen atoms emanating from the cathode produce on the intensity of cathode rays. The writer hopes to make some experiments bearing on this in the near future.

PHYSICAL LABORATORY,
UNIVERSITY OF NEBRASKA.

[1] Phil. Mag. (6), 2, p. 616, 1901.

APPLICATION OF THE HYPOTHESIS OF DISSOLVED ICE TO THE FREEZING OF WATER AND OF DILUTE SOLUTIONS.

BY C. S. HUDSON.

PURPOSE AND INTRODUCTION.

THE belief is becoming general that water is not composed of molecules of the same kind, but rather that molecules of dissolved ice are present in the liquid. The principal evidence for this assumption is the fact that most of the abnormal properties of water, such as its temperatures of maximum density and of minimum compressibility, the increase of its coefficient of thermal expansion with increasing pressure, and its decrease of viscosity under pressure, can be readily explained by the hypothesis that a portion of the water has the same properties that would be ascribed to dissolved ice if the aqueous solution of dissolved ice be analogous to the solutions of most non-electrolytes.[1] It is the purpose of this article to investigate further by means of the methods of thermodynamics this question of dissolved ice, and it may be mentioned in advance that the chief conclusion here obtained is the proof that if we ascribe to the dissolved ice a definite solubility, together with a definite *equilibrium-concentration*, it is possible to account for the constant freezing temperature of pure water and also for the lower freezing points and temperatures of maximum density of dilute aqueous solutions. The first of these results is a matter of rather common knowledge among chemists and physicists,[2] but the other two conclusions are new and constitute further evidence for the hypothesis of dissolved ice.

[1] Röntgen, Ann. d. Physik., **45**, 91–97, 1892; Sutherland, Phil. Mag., 50, 460–489, 1900.

[2] Cf. Bancroft, Journ. Phys. Chem., **2**, 143, 1898; Roozeboom, Zeitschr. physik. Chem., **28**, 289, 1899.

Whether the dissolved ice-molecules that are supposed present in water are identical with the associated molecules of water is unknown and is not essential to the following thermodynamical study. Without making any restriction concerning the formula of the dissolved ice, we will assume that it has the property common to all crystalline solids of crystallizing from solution when the necessary conditions of supersaturation are fulfilled, or in other words that the dissolved ice has a definite solubility which is, like all solubilities, variable with the temperature. Furthermore, if the presence of such a substance dissolved in water and producible from it be assumed, it follows that a state of equilibrium exists between the dissolved ice-molecules and the solvent water-molecules which can be expressed by the equation

$$\underset{\text{(dissolved ice)}}{m(H_2O)_n} \rightleftarrows \underset{\text{(solvent water-molecules)}}{n(H_2O)_m} \qquad (A)$$

where n and m are integers expressing the degree of polymerization of the two substances in terms of the molecule of water-vapor as unit. The state of equilibrium represented by this equation is variable with the temperature and at a given temperature there is a concentration of dissolved ice, here called the *equilibrium-concentration*, which is in equilibrium with unit concentration of solvent water-molecules. At constant temperature and pressure this equilibrium-concentration is invariable for pure water, and an attempt to alter it by direct addition or withdrawal of either of the constituent substances must prove futile, because the system is not composed of two independent components. If these two concentrations of dissolved ice, namely the solubility and the equilibrium-concentration, be assumed, and the laws of dilute solutions be applied to water, a number of results follow, which will be given under the following six headings: (1) The relation of the solubility and equilibrium-concentration curves to the freezing-temperature of pure water, (2) the necessity of a constant freezing-temperature of water, (3) the maximum work obtainable by the freezing of ice from pure water and from a dilute solution, (4) the lower freezing-temperatures of dilute solutions, (5) calculation of the molecular depression of the freezing point by aid of the foregoing hypothesis, (6) the lower temperatures of maximum density of dilute solutions.

1. THE RELATION OF THE SOLUBILITY AND EQUILIBRIUM-CONCENTRATION CURVES TO THE FREEZING-TEMPERATURE OF PURE WATER.

Let the solubility of the dissolved ice in unit concentration of the solvent water-molecules at any given temperature be S, and the equilibrium-concentration at the same temperature be C_{ie}. At temperatures where S is greater than C_{ie}, the dissolved ice does not saturate the solvent, there is no tendency for ice to precipitate, and consequently water is stable at these temperatures. Such temperatures are obviously above the freezing temperature. On the other hand, at temperatures where C_{ie} is greater than S, there is more ice in solution than corresponds to its solubility and this excess can precipitate, the water can freeze. At such temperatures, which are obviously below the freezing-temperature, water can be considered to be a supersaturated solution of ice. It is plain that at the freezing-temperature $C_{ie} = S$. These relations are illustrated by the accompanying diagram, in which the coördinate axes measure temperature and concentration of dissolved ice respectively. The intersection of the curve of solubility, S, with that of equilibrium concentration, C_{ie}, gives the freezing temperature of pure water under ordinary atmospheric pressure. If the pressure be introduced as a third variable and be measured along a third axis perpendicular to the plane of the paper, the S and C_{ie} lines become surfaces and the freezing-temperatures for the various pressures lie on the line of intersection of these two surfaces. How these surfaces change with the pressure is not known, but their intersection, the line of freezing-temperatures, approaches the concentration-axis with increasing pressure, because the freezing-temperature is known to be lowered by pressure.

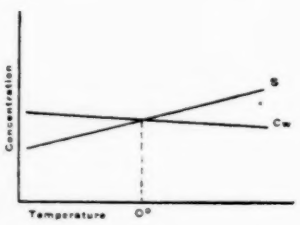


Fig. 1.

2. THE NECESSITY OF A CONSTANT FREEZING-TEMPERATURE.

If an isolated system composed of undercooled water be imagined and the precipitation of some of the excess of dissolved ice be con-

sidered begun, the accompanying evolution of heat will raise the temperature of the system and thus cause the equilibrium-concentration to approach the solubility (compare Fig. 1). Since the process of precipitation causes the rise of temperature, it is evident that the temperature will not rise appreciably beyond a point at which the precipitation ceases, provided the establishment of the new equilibrium-concentration that follows a change of temperature takes place with great rapidity. This limit beyond which the temperature of the freezing water cannot rise is obviously the temperature at which the equilibrium-concentration is equal to the solubility, namely, 0°. That the system will continue to rise toward this limiting temperature so long as undercooled water is present is evident from the relations of Fig. 1, because as long as water below 0° is present in contact with solid ice, the supersaturated solution will precipitate ice and an accompaning rise in temperature will occur.

3. The Maximum Work Obtainable by the Freezing of Ice from Pure Water and from a Dilute Solution.

The formation of ice from water can take place in at least three ways, namely, by distillation, by the freezing of pure water, and by the freezing of a solution. The details of each of these processes will now be considered, the aim being to calculate the maximum work obtainable from the freezing.

A. *Formation of Ice by Isothermal Distillation.* — At the temperature T let the vapor pressure of pure water be P_w and that of ice P_i. Consider the following isothermal and reversible process. n mols (n 18 gr.) of the undercooled water are evaporated at the constant vapor-pressure P_w; the resulting gas is expanded from P_w to P_i, and then condensed to ice. The total work obtainable from the system during the formation of one mol of the ice is

$$W = nRT + nRT \log \frac{P_w}{P_i} - nRT = nRT \log \frac{P_w}{P_i}. \qquad (1)$$

Since the indicated isothermal process is reversible, the work W is the maximum work or free energy of the change.

B. *Formation of Ice by Freezing Pure Water.* — Consider at temperature T a mass of water in equilibrium which contains C_w mols

of ice (nC_{ic} 18 gr.) dissolved in one mol of the solvent water-molecules. By means of an osmotic wall operating so rapidly that no chemical reaction as indicated by equation (A), page 17, takes place during the following physical changes, concentrate the dissolved ice from C_{ic} to S, the solubility of the ice at the temperature T, and then press out the dissolved ice at constant concentration S to form solid ice; the maximum amounts of work obtainable from the system during these two changes are, respectively,

$$W_1 = C_{ic}RT \log \frac{C_{ic}}{S} \text{ and } W_2 = -C_{ic}RT.$$

Although the indicated procedure causes the formation of C_{ic} mols of solid ice, it is to be noticed that the resulting system is not composed of ice and ordinary water, because the original water has been deprived of its dissolved ice and has therefore become unstable. In order to calculate the maximum work that is to be obtained from the changing of this unstable water to the stable form, we proceed as follows: Since the unstable water does not contain the dissolved ice, its vapor-pressure P_u would be expected to be greater than that of the stable water, and would be given by the formula of Raoult,

$$\log \frac{P_u}{P_{ic}} = C_{ic}, \text{ or } \log P_u = \log P_{ic} + C_{ic}.$$

If the mol of unstable water which was produced in forming the ice be evaporated at its vapor-pressure P_u, and the resulting gas be then changed in concentration from P_u to P_{ic} and condensed to form stable water, the desired condition of equilibrium is reached in a reversible manner and the work obtained from the transformation of the unstable water to the stable form is

$$W_3 = RT + RT \log \frac{P_u}{P_{ic}} - RT = RT \log \frac{P_u}{P_{ic}}.$$

If the value of $\log P_u$ that was given above be substituted in the last equation, it is found that $W_3 = C_{ic}RT$. The total work to be obtained from the freezing of stable water to form C_{ic} mols of ice is

$$W_1 + W_2 + W_3 = C_{ic}RT \log \frac{C_{ic}}{S},$$

and the maximum work per mol of ice formed is

$$W = RT \log \frac{C_w}{S}. \qquad (2)$$

C. *Formation of Ice by Freezing a Dilute Solution.* — Imagine at constant temperature T a reservoir made up in the following manner. A dilute aqueous solution is to be in contact with a non-miscible liquid, which shall have the property of dissolving the ice-molecules readily, but not the water-molecules.

Let the vapor pressure of the aqueous solution be P_s and the concentration of the ice in it be C_s; then if the solubility of the ice be S' in the second solvent and S in water, the concentration of ice in the second solvent when the reservoir can be in equilibrium will be $C_s S'/S$. By means of an osmotic wall operating so rapidly that no chemical reaction as given by equation (A), page 17, takes place in the second solvent, draw out from the aqueous solution into the second solvent one mol of dissolved ice at the constant concentration $C_s S'/S$, whereby the work RT is obtained from the system. In order to keep the reservoir in equilibrium during this change, n mols of water are distilled into the aqueous solution while the ice is being drawn out, and by this distillation the work

$$nRT \log \frac{P_w}{P_s}$$

is obtained. At this stage, contact between the two liquids is to be broken and the mol of ice is to be compressed from concentration $C_s S'/S$ to S' and then pressed out of solution at constant concentration S'. During the last two changes the work

$$RT \log \frac{C_s \frac{S'}{S}}{S'} - RT = RT \log \frac{C_s}{S} - RT$$

is produced, and the total work to be obtained from the freezing of one mol of ice in this isothermal and reversible manner is

$$W = RT \log \frac{C_s}{S} + nRT \log \frac{P_w}{P_s}. \qquad (3)$$

4. THE LOWER FREEZING-TEMPERATURES OF DILUTE SOLUTIONS.

If the expressions (1), (2) and (3) of the preceding section for the free energy of the freezing of water to form one mol of ice be placed equal to one another, the following relations are obtained:

$$\frac{C_{w}}{S} = \left(\frac{P_{w}}{P_{i}}\right)^{n}, \tag{4}$$

$$\frac{C_{s}}{S} = \left(\frac{P_{s}}{P_{i}}\right)^{n}, \tag{5}$$

$$\frac{C_{w}}{C_{s}} = \left(\frac{P_{w}}{P_{s}}\right)^{n}, \tag{6}$$

From the last equation it is evident that the equilibrium-concentration for a dilute solution is less than that for pure water at the same temperature, because the vapor-pressure of the solution is less than that of pure water. This conclusion that a dilute solution contains less dissolved ice than does pure water, has an important consequence; for it is therefore evident that a dilute solution can not precipitate ice at the freezing-temperature of water, but must be cooled to a lower temperature in order to cause the concentration of ice in the dilute solution to become equal to the solubility of ice in water.[1] The accompanying figure illustrates the relations which are under consideration. The coördinate axes and the curves S and C_{w} have the same significance as in Fig. 1, and the curve C_{s} represents the equilibrium-concentrations for a dilute solution. The intersection of S with C_{w} represents, as before, the freezing-temperature of pure water, and the intersection of S with C_{s} gives the lower freezing-temperature of the dilute solution.

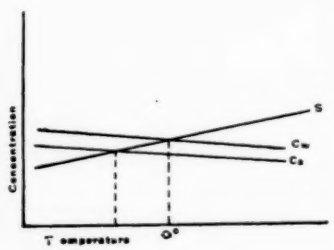


Fig. 2.

[1] It is assumed in drawing this consequence that the solubility of ice in the dilute solution is not appreciably different from its solubility in water.

5. Calculation of the Molecular Depression of the Freezing Temperature from the Foregoing Hypothesis.

Consider a solution containing a mols of foreign substance dissolved in 1,000 grams of water, and let its freezing-temperature be $(273 - dT)$. If $C_{s, dT}$ and S_{dT} represent the equilibrium-concentration and solubility respectively for the solution at its freezing-temperature, the equality $C_{s, dT} = S_{dT}$ holds. If H_s denotes the heat of solution of ice per gram,

$$\log S_{dT} - \log S_0 = + \left(\frac{H_s n \cdot 18}{RT^2} \right) dT,$$

in which S_0 denotes the solubility of ice at zero degrees. This equation can be rearranged to

$$\log S_{dT} = \log S_0 + \frac{H_s n \cdot 18}{RT^2} dT. \qquad (7)$$

Equation (6), page 22, gives the relation

$$n \cdot \log \frac{P_{w, dT}}{P_{s, dT}} = \log \frac{C_{w, dT}}{C_{s, dT}},$$

and since the law of Raoult gives

$$\log \frac{P_{w, dT}}{P_{s, dT}} = \frac{a \cdot 18}{1{,}000},$$

it follows that

$$\log C_{s, dT} = \log C_{w, dT} - n \frac{a \cdot 18}{1{,}000}. \qquad (8)$$

Now if H_T denotes the heat of formation of one gram of the dissolved ice, we have an equation similar to the second one in this section, or,

$$\log C_{w, dT} = \log C_{w, 0} + \frac{H_T n \cdot 18}{RT^2} dT.$$

If this value of $\log C_{w, dT}$ be substituted in equation (8), and the resulting value of $\log C_{s, dT}$ be placed equal to (7), it follows, since $C_{w, 0} = S_0$, that

$$dT = \frac{a \cdot 18}{1{,}000} \cdot \frac{RT^2}{18(H_T - H_s)}.$$

Now the expression $(H_T - H_S)$ is equal to the heat of fusion of one gram of ice, *i*, *e*., *L* calories, or,

$$dT = \frac{a}{1{,}000} \cdot \frac{RT^2}{L}.$$

6. The Lower Temperatures of Maximum Density of Dilute Solutions.

It was first clearly explained by Röntgen (*loc. cit.*) that the occurrence of the temperature of maximum density of water may possibly be due to facts connected with the presence of ice dissolved in the water. According to this view a rise in temperature would cause water to change in volume as the result of the effect of heat both upon the volume of the solvent water-molecules and upon the equilibrium-concentration. The former of these effects is supposed to be an increase of volume with increasing temperature, and the latter, a decrease in equilibrium-concentration and consequently in volume with increasing temperature; and it is obviously possible that these two opposing changes of volume may just neutralize each other at the temperature of maximum density. Röntgen has also shown that the lowering of the temperature of maximum density by increased pressure is a fact in agreement with this view of the cause of the temperature of maximum density; for it would be supposed that the equilibrium-concentration would be diminished by subjecting the water to increased pressure, and therefore the change of volume that is due to the effect of temperature upon the equilibrium-concentration would be correspondingly decreased.

I wish to add to this argument that the fact that solutions have temperatures of maximum density lower than that of pure water is also in complete agreement with the hypothesis of dissolved ice; for if we accept the conclusion of section four that solutions contain less dissolved ice than does pure water, the reasoning of the previous paragraph concerning the change of maximum density with pressure applies also to the influence of dissolved substances upon this temperature. In this connection it is to be emphasized, however, that the temperature of maximum density of a solution cannot be expected to be subject to such simple conditions as is the freezing-temperature of the solution, because the effect of temperature upon

the volume of the dissolved substance, which is a specific property of the solution, must certainly be an important factor in determining the temperature of maximum density. It is even possible that this specific influence of the solute may be great enough in exceptional cases to cause the temperature of maximum density to increase with the concentration of the solution. On the other hand, it can be expected that the majority of dissolved substances will lower the temperature of maximum density, and that equimolal solutions of substances which possess similar chemical and physical properties will have the same temperature of maximum density. This expectation agrees strikingly with the recent measurements of Müller,[1] who found that the lowering of the temperature of maximum density caused by dissolving various organic compounds in water is proportional to the concentration of the solution and has the following values for molal solutions of the different substances, which are here grouped in accordance with their constitutional similarity.

Phenol	7.2°
Pyrocatechin	7.7
Hydroquinone	7.4
Resorcin	7.6
Pyrogallol	8.7
Phloroglucin	7.8
Mannite	11.1
Dextrose	10.1
Oxalic acid	12.2
Succinic acid	12.5
Tartaric acid	15.7

It is obvious that equimolal solutions of substances of similar composition have very nearly the same temperatures of maximum density.

Summary.

The contents of this article may be summarized as follows:

Following the hypothesis advanced by Röntgen in 1890, it has been shown that if cold water contains ice dissolved in it, it is probable that the ice has a definite solubility in the water, and also a definite *equilibrium-concentration*, both of these concentrations varying with the temperature independently.

[1] Zeitschr. physik. Chem., 43, 109–114, 1903.

The assumption of the existence of these two concentrations will account for the constant freezing-temperature of pure water, and this temperature has been shown to be the temperature at which the *equilibrium-concentration* is equal to the solubility.

Three values for the free energy of the freezing of water have been derived, corresponding to the three methods by which the water was frozen, namely, by distillation, by freezing pure water with the aid of an osmotic wall, and by freezing a dilute solution. From the equality of the values of these expressions of the free energy of freezing, it follows that the concentration of ice in a dilute solution is less than the concentration of ice in pure water at the same temperature. It has then been shown how this conclusion will account for the fact that dilute solutions have lower freezing points and lower temperatures of maximum density than pure water, and the formula for the molecular depression of the freezing temperature, $dT = \frac{a}{1{,}000} \cdot \frac{RT^2}{L}$, has been derived from the foregoing hypothesis that water contains ice dissolved in it.

PHYSICAL LABORATORY, PRINCETON UNIVERSITY,
January, 1905.

COLOR IN PLATINUM FILMS.

By Isabelle Stone.

WHILE making platinum films by cathode discharge I found that, using a platinum point as cathode, I obtained colored rings on a glass plate placed directly under the point. In order to investigate this phenomenon, I got together the necessary parts for a receiver of the kind shown in the diagram. The receiver *A* fitted into a circular groove cut out of the aluminum plate *xy*. This aluminum plate contained a binding post *B*, and inside the receiver, two aluminum supports *K* and *L* on which the glass plate *J* rested. Through the neck of the receiver fitted a hollow ground-glass stopper *C*. *C* was in connection with two branch tubes *D* and *E* in each of which fitted ground-glass stopcocks *F* and *G*. Through the top of the ground-glass stopper *C* was fused a loop of platinum wire ending within the receiver in a hook. To the outer loop *H* the wire from the secondary coil was attached. To the inner hook any form of cathode could be suspended. The cathode first used was a thick platinum wire sealed into a glass tube with enough of the wire left at the upper end to form a loop for suspension and two millimeters left at the lower end to form the cathode. The stopcock *G* was turned to shut off the entrance of air and the tube *E* being joined through a drying tube to a pulsometer oil pump, stopcock *F* was left open and the exhaustion of air from the receiver commenced. Later, when it became necessary to measure accurately the pressure of the air in the receiver, the tube *D* was connected to a McLeod gauge by means of the two-way stopcock *G*. The pulsometer oil pump was run by a motor and made about thirty strokes per min-

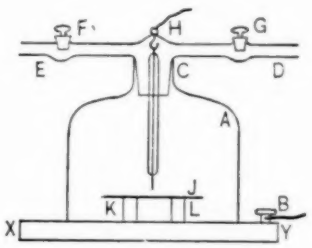


Fig. 1.

ute and by means of it I could get down to a pressure of .3 mm. A wax of rosin and beeswax was used to make the connection between the receiver and the aluminum base. The first fourteen plates were made with no account taken of pressure except that a purple light in the receiver meant a low vacuum and the pale blue light, high vacuum; direct current was used, the alternations brought about by a Wehnelt interrupter and secondary coil. This interrupter was first a thin platinum wire immersed in dilute sulphuric acid; the wire was surrounded by a hard-rubber cylinder except for its tip which dipped in the acid and could be lengthened as it wore away. It was an unsatisfactory interrupter for continuous work, since it could be run for only a minute or two at a time, then would sputter and cease working. However, if rested for a moment and thus allowed to cool, it would again work satisfactorily for a minute or two; thus a summation of effects could be obtained. Later, a solid stick of platinum was substituted for the fine wire and could be used consecutively for an hour or more at a time and in this respect was all that could be desired. But even with the platinum stick interrupter, the current density would change as the point wore away and could not be measured with any accuracy, therefore, in the end the Wehnelt interrupter and coil were given up entirely and a 2,000-volt direct-current dynamo used whose current could be accurately measured at any time. Another improvement consisted in connecting the receiver directly to a mercury pump so that lower pressures could easily be obtained and by connecting the oil pump to the mercury pump, the air could be removed from the receiver quickly and with ease — the pressure was read from a McLeod gauge connected to the mercury pump.

Viewed through the receiver, the glass plate could be watched during the course of the deposit and the general method of formation appeared as follows: A brown spot formed directly under the cathode; this changed gradually into reddish brown, increasing in size; then blue appeared at the center edged with red and beyond the red the brown, later blue increased in area and turned to red, indicating the starting of the second set of colored rings.

It soon became evident that time of discharge and distance between cathode point and glass plate were closely related; the closer the

point to the plate, the shorter the time taken to get good colors and conversely. I also found that with the plate close to, say within 2 mm. of the cathode, the rings were narrow and of small diameter. As the distance was increased the rings spread out in area, became broader and of larger diameter. By varying the distance from 2 to 10 mm., the outside diameter of the rings could be increased from a few millimeters to several centimeters. This was true, whatever the form of cathode used. Also, on changing my cathode from coarse to fine wire, the rings became narrower and of smaller diameter.

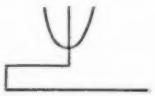
I soon found that pressure played an important part in the formation of the rings and, after the first few films, kept a strict account of that factor.

In my early work I obtained many films that at the time of making could not be accounted for, but showed typical aspects after finding the important part that pressure and distance played. I frequently obtained dim rings, now and then a granular deposit instead of the smooth coating generally gotten and a particular kind of film showing a transparent center surrounded by a black irregular ring often puzzled me, for I was soon led to see that good colored rings had two characteristic appearances. One type showed a faint yellow tinge at the center, the other colored rings were practically transparent and beyond the colors was a wide absolutely transparent zone bounded by a fine black deposit. The other type of good colored rings showed brilliant colors and were absolutely transparent. To account for these two types and to explain variations from them, it was necessary to make many films under varying and measurable conditions.

After the cathode had been used for a time, a heavy platinum coating would collect on the glass surrounding the platinum tip. As this increased, the cathode glow would bend up about the glass, away from the tip. When this occurred, it was hopeless to accomplish anything without great waste of time, for the discharge was made very slowly and most irregularly and the best thing to do was to stop and clean off the glass.

New forms of cathodes were tried. A platinum sphere fused on the end of the heavy platinum wire gave rings like those produced

by the platinum point. By varying the distance between cathode and plate, the same peculiarities in size of ring was noted as with the point cathode. I tried a cathode made of thin platinum wire bent into a circle with the plane of the circle horizontally above the glass plate. The point of joining of the circle to the supporting stem always produced a little distortion of the inner rings; but, in general, under the circular opening of the cathode there was a uniform area of color; the rings were under the wire and followed in outline the bending of the wire; the deposit directly under the wire was thickest, showing a brownish color. In any vertical section of such a cathode, different points of the wire are at different distances from the plate and in consequence the rings farther from the wire are broader than those more directly under the wire. A lack of parallelism between the circle cathode and the plate was indicated by a crescent that occurred in the rings. I gradually bent the circular cathode down until it stood vertically over the plate. Plates were made with the circle at various angles with the vertical. These plates showed the following characteristic; about that part of the wire nearest the plate, the rings were narrowest, taking an elliptical form, the lack of symmetry being on that side where the circle was farthest from the plate. This distortion decreased as the angle made with the vertical was decreased, until when the cathode stood with its plane perpendicular to the plate, all the ellipses were symmetrical. In this series of experiments, there existed in the intermediate stages what might be called a total effect and an effect due to that part of the cathode nearest the plate — the total effect being shown by the bounding elliptical rings and the special effect in the distorted and eccentric ellipses within. When the circular cathode hung perpendicularly to the plate, the special effect merged into the total effect and the plate was covered with perfectly symmetrical ellipses. After observing that an elliptical cathode gave ellipses and a triangular cathode, triangles, I tried for side effects given by the different cathodes standing my plate vertically in the receiver and near to that portion of the cathode to be investigated. Bending my circular cathode, so that its plane stood vertically and also in such a way that the effect of the supporting stem was eliminated, I obtained on a vertical plate, parallel to the cathode plane, circular

rings and on a vertical plate at right angles to the cathode plane, elliptical rings as would be expected. With the elliptical cathode, ellipses were formed whether the vertical plate was placed opposite the side of least or greatest curvature, though, while in the first case, the ellipses were long and narrow, in the second case, they were almost circular; the side effects for the knob cathode were always circles. With a cathode shaped, thus,  and a horizontal plate, I obtained long, narrow ellipses, the length of the ellipse depending on the length of the wire and the width of the ellipse on the diameter of the wire; a plate placed vertically at the left hand end received ellipses and at the right hand end, namely the point, circles were obtained. The same kind of ellipses were obtained from a circular cathode hung horizontally and a vertical plate, no matter where the plate was placed, as in this case the curvature is everywhere the same.

Any change in form of cathode produced a corresponding change in form of rings and in each case, the deposit under that part of the cathode nearest the plate showed a yellow hue; beyond the colored rings was a transparent zone following the outline of the rings and beyond this zone an even black deposit. As previously noted in the case of the circular cathode, it was found that in all cases where the wire was bent into various shapes, a lack of parallelism between the plane of the cathode and the plate was indicated by a crescent of color among the symmetrical rings. Other sources of distortion of rings occurred when the discharge passed to the aluminum supports, when the plate was too small and did not cover the supports, and also when there were irregularities on the cathode. Blemishes sometimes appeared due to testing the discharge at high pressure, especially when the current was strong. In bringing the plate close to the cathode, particularly in obtaining side effects, a portion of the cathode would touch the plate and even if at first the cathode was not touching, it was noticed that as soon as the discharge passed, the cathode would be attracted to the glass and touch it througout the interval of film formation. This touching could always be traced by a transparency of the plate where the contact was, every other part of the plate having a deposit.

From experience with trying to get a half film of platinum on an interferometer plate, working twenty-four hours with the lowest pressure the oil pump would give and getting rectangular rings on the plate (like the shape of the rectangular cathode used), I realized the importance of pressure, so put my receiver on a mercury air pump with which I could obtain pressures of any value desired. I wished to find whether a low pressure produced a uniform field and no color as Mr. Langden had found.[1] With a knob-cathode at a very short distance from the plate and a pressure of about 0.1 mm. I obtained a transparent center surrounded by a black ring and no color. On using a pressure of 1.28 mm. and the same distance (2 mm.) I obtained in three minutes beautiful colored rings, showing the brown tint characteristic previously noted. Taking a given distance, I tried the effect of altering the pressure, using 1.28 mm., 0.9 mm., 0.6 mm., 0.3 mm. and 0.1 mm. pressures. I obtained colors until 0.3 mm. pressure was reached at which there was a heavy deposit, showing a trace of ring formation on the back of the plate. At 0.1 mm. pressure, there was but a slight deposit, center transparent, no color. I then tried altering the distance but taking the same pressures used before. All the charateristics previously noted were obtained. At 0.3 and 0.1 mm. pressure no colors were found but heavier deposits than for the shorter distance. Thus, when the Wehnelt interrupter was used, the minimum pressure for rings seemed to be about 0.3 mm. Then I tried to find the maximum pressure for ring formation taking a fixed distance and varying the pressure from 0.1 mm. as high as I could go and still get color. At 3 mm. pressure there was considerable trace of color, though the deposit was irregular. For good ring formation 2 mm. seemed the maximum pressure when the Wehnelt was used. So I could state that using this interrupter the minimum pressure for rings was 0.3 mm., and the maximum pressure about 2 mm. On using the 2,000-volt dynamo current, these limits were extended, particularly in higher pressures.

It was then clear how Mr. Langden, always working at pressures below 0.1 mm., had always obtained uniform platinum films while

[1] Electrical Resistance of Thin Films Deposited by Kathode Discharge, A. C. Langden, PHYSICAL REVIEW, Vol. XI., July-August, 1900.

the pressures I used (usually exceeding 0.1 mm.) had resulted in colors. Also the explanation of the tiny transparent center, surrounded by a black ring, was clear. This was always obtained at pressures under 0.1 mm. and when the glass was close to the cathode; thus, the plate being within the cathode dark space, received scarcely any of the deposit. On the other hand, at pressures under 0.1 mm., when the distance between cathode and plate was increased, I obtained a heavy, uniform film. However, whenever color was obtained, I found that the cathode dark space had no effect upon my films. When the distance between cathode and plate was small I could get as good rings as for a great distance, though in the first case the plate was far within the cathode dark space and far outside of it in the other case. Also at a pressure of 12 mm., where, using the dynamo, good rings were obtained, there was no light in the receiver except a purple glow about the knob.

As the pressure is increased from .05 mm. up to 5 mm. the following stages may be traced in the films formed between these limits; at .05 mm., the lowest pressure used, there was a heavy platinum deposit; at 0.1 mm. a uniform deposit, but more under the cathode and less spreading than for .05 mm. pressure; at 0.2 mm. a slight trace of color was noticed in the uniform deposit, more frequently on the back of the glass plate; at 0.3 mm. colored rings were formed that were practically transparent and this held up to 1 mm. pressure; at 1 mm. the appearance was that of colored rings slightly yellowish in tint surrounded by a transparent zone and beyond the zone an even black deposit. At 2 mm. pressure, the rings were very perceptibly smaller, the transparent zone correspondingly contracted and the outer black deposit thinner and more transparent; from 2 mm. upward, the decrease in size of rings and transparent zone continued and the increase in the transparency of the film also continued. At a pressure of 12 mm. the rings were very small and practically transparent with no other trace of deposit. The above account applies to films, when the distance between the cathode and plate is from zero to six millimeters. When the distance is ten millimeters, a similar description applies until 1 mm. pressure is reached. At that point, the large rings began to decrease and the transparent zone was small, a greater increase of

pressure resulted in a uniform black film and no color. This heavy deposit continued up to near 2.5 mm. pressure then grew thinner as the pressure was increased, ultimately disappearing. (I had previously noted that often, after a deposit, there was a heavy black coating on the aluminum base of the receiver; this coating was more noticeable when a small glass plate was used, thereby exposing more of the base to the rays; at the same time on the glass, colors, only appeared.) It seems then that transparency is characteristic of low pressure, brown color and boundary zones for a moderately low pressure. For moderately high pressure, two cases exist, depending on the distance of the plate from the cathode and resulting in smaller rings and increase of the black deposit for the shorter distance and heavy black deposit, showing no color for the greater distance. Again for very high pressure there is very little deposit, whatever the distance. The lower the pressure and the greater the distance, the more transparent is the film within the range for good ring formation. The changes occurring in a film, as the pressure is increased from .05 to 5 mm. may be summed up thus: an even black deposit gradually gives way to colored rings; shortly before 1 mm. pressure is reached, the black deposit again appears at the edges of the plate; with greater increase in pressure, the rings decrease in size and the black deposit creeps in toward the colored area, reaches a maximum and at high pressure disappears. When the distance between cathode and plate is small, the colors begin at a higher pressure than in the case where the distance is great and the black deposit at high pressures is not so heavy, nor does it conceal the rings completely. For all distances, the appearance at 1 mm. pressure is characteristic and this may be called the critical pressure. A disturbing element in comparing corresponding films at different distances was due to the glow not being strictly confined to the cathode. If it ran up the glass of the cathode or if a discharge occurred at the top of the receiver, the rings were smaller and took a longer time in formation.

I see no possible explanation of this phenomenon on the basis that the even, black deposits are obtained when the plate is just at the edge of the cathode space, for, while it may apply to results obtained at low pressure, it cannot explain why at high pressure and great

distance an even deposit is obtained. Again, as pressure increases and the glow decreases, the plate nearest the cathode would ultimately touch the edge of the cathode dark space and receive the even deposit which is contrary to the results obtained. It is a curious fact that, for a distance of 10 mm. an even film may be obtained either at .2 mm. pressure or at a pressure ten times as great.

In comparing those films made by using the Wehnelt interrupter with those made by the current from the two thousand volt dynamo, it is interesting to note that the two classes are really one and the same; for a given pressure and distance, the appearance of the resulting film is the same in either case.

The attempt was made to arrive at the same stage with each film; let us say the starting of the second set of rings. This could be observed from outside the receiver when the light was good. One could see the brown spot form under the cathode, could see it turning to red, then to blue and then to brownish red again, thus indicating the starting of the second set of rings. Under these circumstances, it was possible to make comparison of the time taken at the different pressures to reach this stage. Although one must keep in mind the fact that an increase in distance between cathode and plate means an increase in time, since the size of the rings is correspondingly increased, nevertheless one can say that in any set of films where the distance is unchanged the time taken to reach the given stage of film formation is the same from the lowest pressure giving rings up to the pressure where the even deposit starts to decrease. Beyond this pressure, the time is increased. Suppose the time of formation between 0.3 mm. and 2 mm. pressure is ten minutes, the time taken to reach the same stage in the rings from 2–5 mm. pressure is almost twenty minutes and beyond 5 mm. pressure, the time is enormously increased, two hours and a half being necessary for a film at 12 mm. pressure. In this connection, it should be stated that films made with the interrupter took a longer time than exactly similar ones made by the current from the dynamo.

To be able to measure the current flowing through my receiver and the fall of potential between anode and cathode, at any chosen pressure, I put an ammeter reading to .001 ampere in the main cir-

cuit and a static quadrant electrometer between anode and cathode. Beginning with the highest pressure used and letting the discharge pass through the receiver, I read the current and voltage for that pressure; taking a stroke of the pump, I again read the three corresponding values. In this way I proceeded by steps to the lowest pressure used in the work. The discharge passed continuously between cathode and plate during this experiment, the accompanying curves give the relation between pressure and voltage and pressure and current respectively and show that down to a pressure of about 1 mm. the current and also the voltage is practically constant; between 1 mm. and the lowest pressure used, a slight decrease in

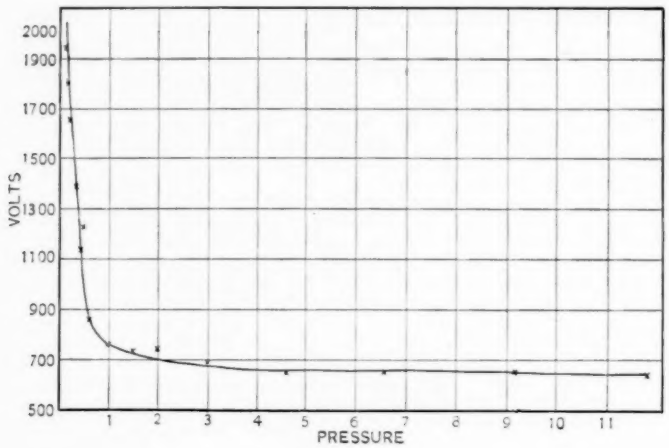


Fig. 3.

pressure is accompanied by great increase in potential and corresponding decrease in current. At four separate times such a series of values were taken and curves constructed (Figs. 3 and 4). In two trials the voltage was constant at about 650 volts and the current constant at .005 ampere until a pressure of 1 mm. was reached; then the current fell steadily to .001 ampere and the voltage rose to 1,950 volts; in a third trial, starting with .004 ampere and 600 volts, both factors remained constant until the pressure was decreased to 1 mm.; between 1 and 0.5 mm. pressure the change was slight, but below 0.5 mm. the current fell to .001 ampere and potential rose to 1,750 volts; a fourth trial started with a current of .001 ampere

and voltage of 550, both remained constant until 0.5 mm. pressure was reached; then came the sudden drop of current to .0001 ampere and rise of potential to 1,730 volts. Evidently the critical point in pressure for these platinum films is lowered by using a lower voltage and current. If the object is not the lowering of the critical pressure, it is of course far better to use a stronger current and shorten the time of deposit. The current usually used in depositing these films was .004 ampere. In comparing the films by reference to these curves, one finds that the uniform films at pressures below 0.1 mm. are formed when the curve is practically ver-

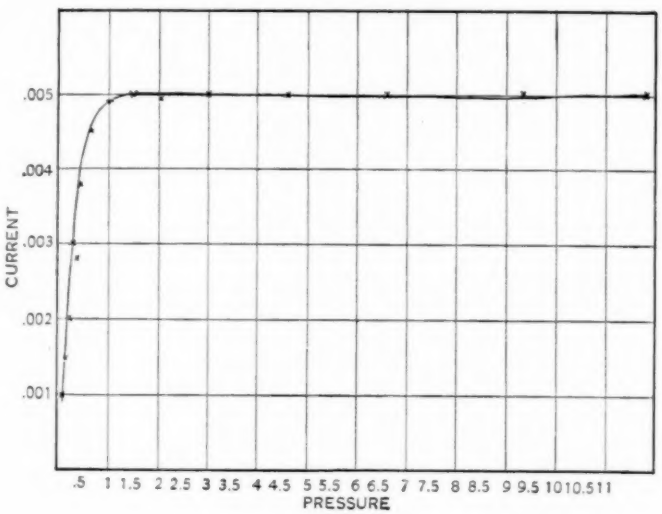


Fig. 4.

tical; that the colored rings showing greatest transparency and free from all uniform deposits are made when the curve shows a rapid decrease of voltage and rise of current and that the deposit is heavier for those films made at pressures above 1 mm. where the curve exhibits itself as a horizontal line. Beyond 3 mm. the decrease in deposit is due to increase in pressure as indicated by the slight glow about the cathode. From observing the curves, I could understand why in the region of pressures below 1 mm., there would be great fluctuations of voltage, for the small increase in pressure due to gases coming off the cathode at the time of dis-

charge. Also if a discharge took place at the platinum hook on which the cathode was suspended, the voltage would drop and the current rise, and if, because of the coating with platinum of the glass about the cathode, the glow ran up the glass, again a change would occur. In connection with these curves it is interesting to note that the test plate used in such an experiment became covered with very large rings showing six or seven alternations of color and the deposit of considerable thickness, thus increase of time of deposit would result in the formation of many rings spreading over the surface of the plate.

In order to prove that the colors would form when a gas other than air was used, I arranged to make the deposit in hydrogen. In the first set of films made by the interrupter, I introduced into the receiver hydrogen generated by the action of acid on zinc and dried by passing it through sulphuric acid and phosphorus pentoxide. I pumped this gas through the receiver three or four times before the discharge passed and thus I made a half dozen plates at varying pressures, in each case rings were formed just as in the case of air. To make sure that I had gotten rid of the gases occluded by the cathode and on the walls of the receiver, I resolved to let the discharge using current from the dynamo pass for some time until the pressure of the hydrogen was stationary as indicated by the gauge. Since, with the preliminary discharge, the glass surrounding the cathode would become coated with platinum and in consequence the glow would bend up about the coated glass, it was necessary to protect the glass during the preliminary discharge. Two pieces of mica were taken and bent so as to surround the cathode above and below, shielding the glass about the cathode and the glass plate. Each of these pieces of mica being wound externally with iron wire was removed when the time came by a magnet outside the receiver. These covers having been fitted around the cathode and the receiver made air tight and connected with the pump, the air was exhausted to a low pressure, C. P. hydrogen was admitted and the pressure again reduced. In this way, hydrogen was admitted three times; then the discharge was allowed to pass for two hours. This process was again repeated and during the second discharge, the gauge was watched. At the end of two hours, when the gauge showed no increase of pressure,

the mica covers were removed from without and the discharge allowed to pass onto the glass plate for twenty minutes, the pressure being 1 mm. The rings were like those obtained at the same pressure in air.

I had made attempts to find the thickness of the films by the micrometer calipers, the measurements, however, were of no value even for thick films because of the uneven thickness of the glass and for thin films I obtained negative values.

I then tried weighing a microscope cover glass, putting on a thin film, reweighing and calculating the average thickness of the film from weight, average diameter of circles and density of platinum. By this method, I found the average thickness equal to .000136 mm. or the thickness of Newton's first bright ring (.000142) approxmately. As this was an attempt to discover how the platinum was deposited on the plate and as I had found that direct observation under the microscope gave me interesting results, I abandoned the weighing method and examined the films one by one under a microscope. When traces of particles were found, the plates were prepared with Canada balsam and cover glasses for use with a high power oil immersion objective. The microscope was then put in front of a lantern and the magnified image obtained on a screen. By running the plate horizontally and vertically, it was possible to examine the whole area and photograph any part of it. Some photographs were taken with objects magnified to 2,000 diameters, others to 2,500 diameters. A film made at a pressure of .2 mm. showed a field of perfectly spherical particles varying in diameter from .0005 to .0009 mm. Apparently there was no symmetrical grouping of particles; some were alone, others in large or small groups and here and there an area quite free from them. Each globule was surrounded by a halo. In other films I found many clusters in various stages of development, several globules collected in a faint halo-like area; again a union of many into a rather irregular crystalline appearing area and finally the merging of masses of these crystalline areas into a large solid appearing mass, surrounded frequently by a brown fringe; the photographs illustrate these stages. The thick films shut off most of the light from the lantern and were uniform except where a tear showed the existence of a continuous yellow layer or here and there a crystal-

line area appeared. Since many of the thin films appeared transparent and the thick ones showed an even yellow deposit, my photographs, for the most part, represented those films where the particles had not yet clustered together to form a continuous film or were taken on the outskirts of the colored area, where the stages of formation could best be observed. Frequently crystalline areas appeared on a uniform field, indicating that particles had been thrown off irregularly after the film proper had formed.

The following explanation seems to fit the observed facts: during the first few minutes of the discharge the platinum thrown off from the cathode is in the form of globules, separated from each other or slightly grouped, hence the deposit appears red; as the discharge continues more globules are deposited, there is a joining together of the groups and the deposit appears blue, edged with red. This, then, would explain the formation of the first set of rings; the center made up of particles close together, the outskirts containing only separate particles. This process is repeated, the thin, transparent film serving as a base for deposit; again particles increase directly under the cathode, first, separated from one another and we have red, then uniting together and we have blue; thus a second set of rings have been formed. As this continues, the rings spread out over the surface of the plate and it is evident why extremely thin films and the outer boundary of the colored area, alone exhibit the separate particles.

The particles may be of different sizes; the change in color depends not on the size, but on the grouping of the particles.

It is my intention to examine films showing the first red color and compare with others in which blue first appears; to investigate farther into the formation of even films at great distance and high pressure and to examine the phenomena produced by a cathode of material different from platinum.

I wish the opportunity to express my gratitude to Dr. Hallock for making this investigation possible for me at Columbia University and for his great liberality and kindness to me throughout the accomplishment of the work. I am also greatly indebted to Dr. Davis, Dr. Tufts, Dr. Pegram and Dr. Forbes for valuable advice and for assistance many times.

Vassar College.

PLATE I.
(To face page 40.)

Color in Platinum Films.
STONE.

THE MAGNETIC ROTATION OF SODIUM VAPOR.

By R. W. Wood and H. W. Springsteen.

Introduction.

In 1811 Arogo[1] discovered that rotation of the plane of polarization occurs when plane polarized light is transmitted through quartz in the direction of its optic axis. This was followed by the careful investigations of Biot,[2] which led him to the deduction of his three well-known laws. That the phenomenon was not confined to solids alone, but occurred also with liquids and gases, was soon made evident by the work of Biot, Sir J. Herschel, Brewster, Faraday and others. Then followed Faraday's discovery[3] that the plane of polarization is rotated by isotropic substances when placed in a magnetic field.

After the discovery by Fox Talbot,[4] about 1840, of the existence of anomalous dispersion, this phenomenon was looked for in the rotatory dispersion of optically-active substances. Biot,[5] Arndtsen,[6] Landolt,[7] Nasini and Gennari,[8] Cotton[9] and others observed anomalous rotatory dispersion in various natural active liquids.

It was natural to expect that this anomaly might also exist in magnetically active substances; several investigators have studied various substances with results not altogether concordant. Becquerel[10] in 1880 observed the effect in oxygen, but others have

[1] Arago, Oeuvres Completes, Tom. X., p. 35, 1812.

[2] Biot, Ann. de Chimie et de Physique, 1815.

[3] Faraday, Experimental Researches (XIXth series), Vol. III., p. 1; Phil. Trans., p. 1, 1846.

[4] Talbot, see Tait's Light, 196, and Proc. Roy. Soc. Edinburgh, 1870–71.

[5] Biot, Ann. de Chimie et de Physique (3), 10, p. 5, 1844.

[6] Arndtsen, Ann. de Chimie et de Physique (3), 54, p. 403, 1858.

[7] Landolt, Beibl., 5, p. 298, 1881.

[8] Nasini and Gennari, Zeitschr. fur phys. Chemie, 19, p. 113, 1896.

[9] Cotton, Ann. de Chimie et de Physique (7), 8, p. 347, 1876.

[10] Becquerel, Compt. Rend., 90, p. 1407, 1880.

been unable to confirm his results. Macaluso and Corbino[1] worked with sodium vapor and found that the rotation was positive, and abnormally great, on each side of the *D* absorption bands, but had a small positive value inside the band. Zeeman[2] also, with a flame between magnet poles, investigated the rotation with highly rarified vapor in the vicinity of the *D* lines and obtained a positive rotation just outside the two *D* lines and a very great negative rotation inside each of them, or rather between the components into which the magnetic field divides the line.

Results published by Schmauss in the Annalen du Physik during the year 1903 appeared to show that the rotatory dispersion is anomalous in the vicinity of the absorption band. He worked with alcoholic solutions of the analine dyes, and with didymium glass, obtaining curves not unlike the anomalous dispersion curves of these substances. His work was repeated by Bates[3] who failed to find any effect whatever due to the addition of the dye, and one of the present writers, has been unable to observe any trace of magnetic rotation in the case of thin plates of solid cyanine in very intense magnetic fields, although a saturated solution of praseodymium chloride appears to show the effect.

In the case of sodium vapor we know positively that the rotation is not anomalous, having the same value for wave-lengths symmetrically situated to the right and left of the *D* lines.

The subject is of much interest theoretically, for the rotation formula developed from the hypothesis of molecular currents[4] calls for an anomalous effect, while the one obtained by considering the "Hall-effect," *i. e.*, the ponderomotive force exerted upon an electron moving in a magnetic field, represents, qualitatively at least, the condition found in the case of sodium vapor.

It was with a view of testing this formula quantitatively that the experiments about to be described were undertaken.

To test a formula we require observations over a fairly wide range of wave-lengths.

[1] Macaluso and Corbino, Compt. Rend., 127, p. 548, 1898.
[2] Zeeman, Proc. Roy. Acad. of Amsterdam, 1902.
[3] See Annalen du Physik., Dec., 1903.
[4] See Drude's Optics.

In the course of some work upon the dispersion of the vapor of metallic sodium, it was found by one of us, that the vapor possesses an enormous rotatory power, even for wave-lengths considerably removed from the D lines, when placed in a strong magnetic field.

It was at once recognized that by employing this medium, the rotatory dispersion formula

$$\delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\lambda^2}{(\lambda^2 - \lambda_m{}^2)^2}\right)$$

could be tested.

That it represents the dispersion qualitatively is clear from the occurrence of the term $(\lambda^2 - \lambda_m{}^2)^2$ in the denominator, for $\lambda^2 - \lambda_m{}^2$ changes sign when we cross the absorption band, and it is this change of sign which gives us the anomalous dispersion. In the present case, however, the squaring of the term gives us the same sign on opposite sides of the absorption band, which calls for a dispersion curve of the type shown in Fig. 1. A curve of this type was obtained by Cotton, but his observations were made with flames, and the effect could only be traced to a very small distance to the right and left of the D lines.

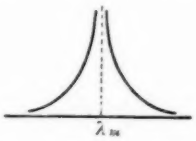


Fig. 1.

We can modify the above formula somewhat in the case of sodium vapor as will be shown later on in the paper.

Apparatus and Method.

The sodium vapor obtained by heating a salt of sodium in a flame is necessarily very rare, and with such a vapor as is well known, the rotation only very near the D lines is perceptible. In order to obtain greater rotations it is obvious that denser vapor must be employed. This was accomplished by heating with a Bunsen flame pure sodium in an exhaused glass tube. This tube, of hard Jena glass, had a length of 25 cm. and an inside diameter of 1.3 cm. Over this and occupying a position midway between the ends of the glass tube was a brass tube 8.2 cm. in length and of such a diameter that it would slide easily over the glass tube. A solid cylin-

drical piece of pure sodium of the same length as the brass tube, and having a diameter of 0.6 cm. was prepared in the following way. A good-sized piece of sodium was melted in an iron crucible over a Bunsen flame, and the molten metal poured into an iron cylinder. This cylinder had a tight fitting iron piston which, when pressed in by squeezing it in a vice, forced the sodium out through a small hole in the end, and the desired length being then cut off. The sodium stick was then placed in the center of the glass tube as quickly as possible to prevent the moist air from coming in contact with it, and the ends of the tube closed with thin pieces of plate glass, cemented on. The glass ends were tested in the magnetic field employed for the experiment, but no rotation due to them could be detected.

Directly over the sodium and inside the glass tube was a thermos element made of iron and constatin fused together; the terminals passing out through a fine glass tube at one end of the sodium

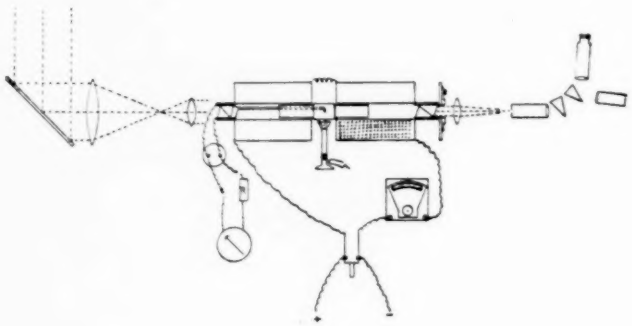


Fig. 2.

tube. Passing through the other end was a tube of small diameter which was connected to an air-pump and sealed off after exhausting the tube. The vacuum used was about one tenth of a mm. of mercury. The sodium tube was then placed inside a Ruhmhorff magnet as shown in the figure, so that the part of the tube containing the sodium was between the poles of the magnet. The magnet possessed the usual nicol prisms, one at each end, the analyzing one being provided with a rotating arm and scale which could be read to tenths of a degree. The wires from the thermo-

element passed out alongside the latter nicol, and communicated with a galvanometer and two other thermo-elements, one of iron and copper and the other constantin and copper. These two elements were placed side by side in a kerosene bath and kept at constant temperature. Directly beneath the center of the brass tube was a Bunsen burner, the height of which was so regulated as to produce the required temperature of the vapor, as determined by the scale-reading of the galvanometer. The brass tube served to distribute the heat from the flame more evenly than could otherwise have been done, and by this means the vapor was kept at a very uniform density.

A 110-volt circuit was connected to the magnet through a double-knife switch, rheostat and ammeter. Since the magnet coils were made of very large wire, a heavy current could be used and the rheostat was adjusted until the current was 35 amperes, and all the observations were made with this current through the magnet. The current, of course, heated the magnet somewhat, but after a short time this heating became fairly steady and with a constant current, the variation in the field-strength introduced no more error than the errors of observation. The strength of the field was determined by measuring the rotation for *D* light which a tube of carbon bisulphide, 8.2 cm. in length, produced. The average rotation obtained was 16°.0. Assuming 0.042 in minutes of arc as the value of Verdet's constant, this rotation of 16° corresponds to a field strength of 2,790 C.G.S. units.

Considerable difficulty was experienced in trying to obtain a sufficiently intense beam of light. The light had to pass through various optical parts and also the dense vapor so that finally only a small percentage of the incident light succeeded in getting through the apparatus. As first tried, the light from an arc was brought to a focus just in front of the polarizing nicol, and after passing through this and the sodium vapor, it could be completely extinguished by the analyzing nicol. Just in front of the analyzing nicol was placed a transmission grating of 14,000 lines and when the nicols were parallel, a bright spectrum was produced in the first order. When the nicols were crossed, the spectrum entirely disappeared. The sodium was now slowly heated, and with the

nicols parallel, the D absorption band slowly appeared, becoming wider and wider as the vapor became denser.

The nicols were now crossed and when the current was turned on, the light was immediately restored for a considerable distance on each side of the D absorption band. It also seemed as if there was a restoration of the light in the part of the spectrum corresponding to the position of the fluted absorption bands, but it was not possible to be sure, with this arrangement of the apparatus. If the analyzing nicol was now slowly turned in a direction which indicated a positive rotation, there appeared two broad black bands, one on each side of the D band. As the nicol was rotated more and more, these bands narrowed up moving closer and closer to the edges of the D band, until finally they reached it. This showed that the rotation was positive on both sides of the D band, and by the readings of the nicol, it was seen that the rotation was very great close to the edges of the D band, but that it rapidly decreased for points further and further away. By using less dense vapor and a reflection grating mounted on a spectrometer, it was possible to see in the second order that the rotation was also positive between the two D lines, but the light here was too faint to permit of a very accurate determination of its amount. It was now necessary to devise some means of determining the wave-length cut out by the black band as the nicol was rotated. To effect this, the light from the arc was focussed on a slit and then made parallel by a collimating lens before it passed through the first nicol. After emerging from the second nicol, it then fell upon a plane reflection grating and into the telescope of the spectrometer. Then the light from a helium tube and a mercury tube was sent through at the same time by means of a small right-angled prism placed on the slit of the collimator, with the intention of using their characteristic lines as reference points from which to measure wave-lengths. But it was found impossible to make the lines appear sufficiently bright and the use of these tubes was abandoned.

Next the sunlight from the heliostat was substituted for the arc, with the hope that the Fraunhofer lines might be sharp enough to be used. But these too, proved to be too indistinct to be employed.

The next method tried was the following: sunlight was focussed on the slit of a monochromatic illuminator and light of the desired wave-length then transmitted through the first nicol, the sodium and the analyzing nicol in turn. The latter was then rotated until the light appeared to the eye, to be entirely extinguished. By this means the rotation for different wave-lengths was obtained at some distance on either side of the *D* band, but when settings were made in its vicinity, the source of light could not be made monochromatic enough, even with the slits of the monochromatic illuminator very narrow, since the magnetic rotation in this vicinity is very great, and although the nicol might be turned so as to extinguish light of one wave-length, light of other wave-lengths would still pass through. With this arrangement, however, the rotation was measured for wave-lengths rather distant from the *D* band and readings were taken until the restored light became too feeble to make the settings accurate.

For the vicinity of the *D* band another method was found which proved very satisfactory. A beam of sunlight from a heliostat was sent through the nicols and sodium tube and focussed upon the slit of a two-prism spectroscope which possessed a resolving power sufficient to separate the *D* lines. By this means the Fraunhofer lines were in sharp focus. An auxiliary scale reflected into the field of view, appeared superposed on the solar spectrum.

With the nicols parallel and the vapor of the right density, not only was the *D* absorption band visible, but also the red and blue channelled absorption bands were very strong. When the nicols were crossed, the field was dark, but when the current was turned on, the spectrum brightened up, not only on each side of the *D* band, gradually shading off in intensity, but also in the red and blue-green. As many as eight distinct red, and eight blue, bright lines were counted. These bright lines apparently coincided with the red and blue absorption bands of sodium vapor, and showed conclusively that the red and blue absorption bands have also a very marked effect on the magnetic rotation.

The bright blue lines due to magnetic rotation were much fainter than the red and it was noticed that when the vapor was of small density, the bright lines in the red appeared, but no trace was seen

of those in the blue-green region. This indicates that the rotation is greater for the red lines than for the blue ones. The absorption lines appear, however, in the greenish blue at a smaller vapor density than that necessary for the appearance of the red absorption bands.

The nicol was rotated and the position of the black bands noted with reference to the spectroscope scale. The position of the nicol was read and the temperature of the vapor recorded. The readings were always taken with a constant current through the magnet. Throughout the experiment the temperature of the vapor remained nearly constant. It is clear that the black bands mark the wave-lengths, for which the rotation is represented by the angle through which the nicol has been turned from its original position of extinction.

The results obtained are recorded in the following table, which is for wave-lengths on the green side of the absorption band.

λ	δ		
	Observed.	Calculated.	
5,886	2,371°	2,285	
5,884	1,185	1,016	
5,876	247	186	
5,875	205	162	$\lambda_1 = 5{,}890$
5,870	107	91	
5,861	49	40.6	
5,844	14.8	15.2	
5,835	10.8	10.9	
5,820	6.5	6.9	
5,805	4.8	4.8	
* 5,770	2	2.5	$\lambda_1 = 5{,}893$
* 5,725	1.4	1.4	
* 5,690	1.2	1	
* 5,660	1.0	—	
* 5,630	0.6	—	
* 5,600	0.4	0.5	

The readings marked with an asterisk were made with the monochromatic illuminator, the others by observing the position of the dark band in the continuous spectrum, which appears the moment the second nicol is turned from its position of extinction. The high values for the first five wave-lengths, were obtained by making observations with a grating, using a vapor of small density, and then

enlarging them to the scale of the density of the vapor used in the other experiments. The rotations on the red side of the D lines are similar for wave-lengths similarly located, in other words the curve is symmetrical. The complete curve is shown in Fig. 3.

It is probable that the complete curve is far from accurate as a whole, for it was constructed from different sets of readings. Moreover the density of the vapor is apt to change during the time occupied in observing and recording a single series.

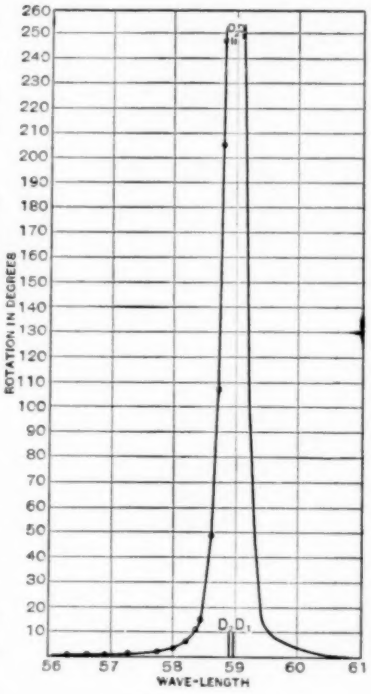


Fig. 3.

At the present time experiments are being made by one of us with a photographic method, which it is expected will yield far more accurate results.[1]

Proof of the Rotatory Dispersion Formula.

In the complete formula

$$\delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\lambda^2}{(\lambda^2 - \lambda_m^2)^2}\right)$$

the first term in the parentheses represents the effect of electrons with periods in the ultra violet. The dispersion of sodium vapor has been shown by one of the writers to be represented by the formula

$$n^2 = 1 + \frac{b\lambda^2}{\lambda^2 - \lambda_m^2},$$

in other words the electrons which cause the D lines are alone operative. We can thus safely assume that the rotation is influenced only by these same electrons, in other words we may neglect the

[1] These measurements have been repeated with a 14-foot concave grating, not only on each side of, but also between the D lines. The rotating lines in the red and blue green region, to the number of 150 have been accurately measured with the same grating. The results will appear shortly in the Philosophical Magazine. R. W. W.

term a/λ^2. The effects contributed by the absorption bands in the blue-green and red can be left out of account as they are but very small. Moreover in the case of sodium vapor n does not differ greatly from unity, except very near the D lines. We can therefore write the formula for the rotation

$$\delta = \frac{b\lambda^2}{(\lambda^2 - \lambda_m^2)^2}$$

and determine the constant b from a single observed rotation.

It is clear that the term $\lambda^2/(\lambda^2 - \lambda_m^2)^2$ will change with changing wave-length much more rapidly than the term $\lambda^2/(\lambda^2 - \lambda_m^2)$ (which occurs in the ordinary dispersion formula); the rotatory dispersion curve will consequently be much steeper than the dispersion curve, as will be readily seen by comparing the curve shown in Fig. 3, with the dispersion curve obtained by Wood for sodium vapor.[1] In calculating the rotations λ_m was given the mean value of the D lines 5,893 in the case of the remotor wave-lengths, and the value 5,890 in the case of those near the absorption. This is an approximation method of course, but it was found to work fairly well in the case of the dispersion of the vapor. The calculated results agree fairly well with the observed, except for the immediate vicinity of the D lines, where they are for the most part too low.

A series of readings were taken with improved apparatus, using a diffraction grating, and measuring the position of the band with a filar micrometer. These observations were made as rapidly as possible to avoid changes in the density, which, as has been already said, are probably responsible for most of the errors. The constant was calculated from the rotation observed for wave-length 5,839.

λ	δ		
	Observed.	Calculated.	
5,875	95°	87.2	
5,886	36	38.7	Constant $b = 113{,}382$
5,875	23	21.7	$\lambda_m = 5{,}893$
5,839	9.5	9.5	
5,821	5	5.4	
5,803	3	3.4	

[1] Phil. Mag., Sept., 1904.

and the observed and calculated values compared. The results are recorded in the opposite table, and indicate that the rotatory dispersion is probably represented by the formula given above.

More accurate results are expected with the photographic apparatus, which will enable the position of the dark bands to be rapidly recorded for different settings of the nicol. The maesurements can then be made at leisure.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

NOTE ON FLEETING AND PERSISTENT NUCLEI IN ENERGIZED DUST-FREE AIR.[1]

BY C. BARUS.

1. *Fog Limits of Fleeting Nuclei.* — The mean increment of nucleation, δN, per centim. of increment of pressure difference, δp, varies very rapidly as compared with the fog limit, δp_0, so long as the reference is to the interval of large variation. It makes no difference by what radiation the nucleation is produced (X-rays or other radiation), $\delta N/\delta(\delta p)$ is rapidly larger as the intensity of ionization is greater, while δp_0 becomes slowly smaller within the interval in question. Below the fog limit of air, and slightly above the fog limit of the ionized medium, the following data are typical. N_{21} shows the number of nuclei caught when $\delta p = 21$ cm., which lies within the pressure interval stated. D is the distance of the sealed aluminum tube, containing radium (.1 g.), from the fog chamber.

Radium (10,000 ×)	$D = 200$ cm.	$\delta p_0 = (20.5)$	$10^{-3}N_{21} = 1$	$10^{-3}\delta N/\delta(\delta p) = 4$
	50	20.4	5	9
	25	20.3	10	(14)
	0	20.1	18	20
X-rays.	200 cm.	20.3	10	16
	50	(20.1)	22	(24)
	10	(19.7)	45	(33)
	5	19.6	50	36

The full N curves are best given graphically. Data for the radium at $D = 100 - 200$ cm. are scarcely distinguishable from air except near the

[1] Read by title at the Chicago Meeting of the Physical Society, April 22, 1905. For earlier observations see Science, XXI., p. 275, 1905; *ibid.*, XXI., p. 563, 1905; Am. Journ. Sci. (4), XIX., p. 349, 1905.

fog limit; for radium at $D = 10 - 25$ cm. they lie close together, above the former and below the data for $D = 0$. With these the X-ray effects at $D = 10 - 50$ cm. are in sequence. Thus there is general continuity between the air curves, the radium curves and the X-ray curves. As a whole the curves for N and δp are doubly inflected: relatively large nuclei are rapidly fewer in number as δp decreases, relatively small nuclei are also rapidly fewer in number as δp increases. Nevertheless the efficient nuclei of intermediate dimensions are of all sizes, while this size tends to become more uniform as the ionization is greater, *i. e.*, the slopes of the curves become steeper. Gradation is accentuated for the case of weak ionization.

2. *Decay of Fleeting Nuclei.* — If N is expressed in thousands of nuclei per cub. centim. and the time of decay t in seconds and if $1/N = a + bt$ so that $dN/dt = -bN^2$ the datum $b = .002$ reproduces the decay curves moderately well, except at the beginning ($t < 30$ sec.), where the observed data are steeper.

3. *Generation and Decay of Persistent Nuclei.* — First exhaustion data of the generation of persistent nuclei are difficult to obtain because the coronas soon become heavy fogs, distorted beyond recognition, and the fog limits variable over wide limits often approaching vanishing smallness. The number of persistent nuclei generated varies with the time of exposure at an accelerated rate as if the nuclei themselves assisted in the generation. For instance at $\delta p = 19.7$ cm., after the times of exposure 1, 2, 3 minutes the nucleations were $N \times 10^{-3}$ 22, 77 (120), respectively.

If N be expressed in thousands of nuclei per cubic centimeter, if t is the time of decay in seconds, and if $1/N = a + bt$ (for which there is here no experimental justification, and which serves only for systematic comparison with the preceding case), the data show that $b = .000013$, *i. e.*, over 200 times smaller than in § 2.

4. *Solution of Fleeting Nuclei (Ions).* — Further experiments in the wooden fog chamber showed that 25–50 per cent. of the fleeting nuclei could be caught and made stable on solution. The mean datum of all results irrespective of the time interval (the effect of which within a few minutes is probably inappreciable) is a preservation of 39 per cent. on re-evaporation of the originally fleeting nuclei from the fog particles condensed on them. In the absence of subsidence of fog (which can not here be allowed for) the result would be larger. In the glass fog chamber which could be made rigorously free from leakage but in which the subsidence loss was greater, 20 per cent. persisted, while all but 2–5 per cent. were lost in 1 minute in the absence of solution. Persisting in the 1–3 minutes following evaporation was not appreciably different, indicating long periods of decay.

5. *Solutional Enlargement of the Nuclei in Dust-free Air.* — The most

interesting case observed is the marked decrement of the fog limit of dust free air producible by solution of the nuclei. Let the first exhaustion be made decidedly above the fog limit (say here at $\delta p = 23$ cm.), to obtain a corona of appreciable size. On evaporating the fog particles, let the second exhaustion be made decidedly below the fog limit (say at $\delta p = 21$ cm.). A large corona, which would otherwise be quite absent, will be observed. Within 3 minutes about 25 per cent. of the nuclei are found to persist. After 10 minutes not more than 5 per cent. were left.

6. *Cause of Periodicity.*[1] — In cases of alternations of large and small coronas, whether the persistence be attributed to electrical potential or to solution, a water nucleus is always in question. Small fog particles are caught on small nuclei near the limit of exhaustion and these evaporate and become the water nuclei available for the next exhaustion. In general there are three groups of nuclei x, y, z, concerned in an exhaustion: a group x of water nuclei from the preceding exhaustion; a group z, which will evaporate to make the water nuclei of the succeeding exhaustion; finally the group y comprising the efficient nuclei of the exhaustion in question. In case of periodicity the successive exhaustions follow the scheme

Exhaustion	1		y_1	z_1	Superior corona on y_1
	2	$x_2 = z_1$		$z_2 = 0$	Inferior corona on z_1
	3	$x_3 = z_2 = 0$	$y_2 + y_3$	z_3	Superior corona on $y_2 + y_3$
	4	$x_4 = z_3$		$z_4 = 0$	Inferior corona on z_3
	5	$x_5 = z_4 = 0$	$y_4 + y_5$	z_5	Superior corona in $y_4 + y_5$
			etc.		

All the details observed with alternations, are thus explained. In view of the rapidity of decay the corona will be formed on the saturation value of $y_n + y_{n+1}$.

7. *Persistence in General.* — This may reasonably be ascribed to the formation of water nuclei, a point of view carried out in my memoir on the structure of the nucleus (Smithsonian Contributions, No. 1373, 1903), but much enhanced by the data of the present investigation. The heavy rains accompanying condensation in case of the persistent X-ray nuclei, are attributable to spontaneous condensation without supersaturation, the nucleus acting under intense X-radiation like a hygroscopic solute. The same result may follow the action of ultra-violet light, as it certainly must result from the presence of phosphorus and of sulphuric acid nuclei.

8. *Distance Effect in Case of X-rays.* — The behavior of the wooden fog chamber in relation to rays coming from different distances being such as if the circumambient medium were equally energised with some-

[1] Cf. Am. Jour. Sci. (4), XIX., p. 349, 1905.

thing recalling the character galvanic polarization, throughout, the following mean data are designed to throw further light upon this behavior. D is the distance of the bulb from the fog chamber. The exhaustion is at the fog limit of dust free air.

Fog chamber	$D=$ 6	50	200	600 cm.	
Wood, lead-cased	$10^{-3}N=$ 50		50	38	
Glass, walls, .3 cm., bottom 1.0 cm. thick	70		41	22	
	55		34	14	
Glass cased in close-fitting lead tube prolonged 50 cm. toward bulb	–	52[1]	25	12	cm.

Media pervious with difficulty eliminate the secondary radiation entering the broadsides and to close the end towards the bulb is to eliminate nearly all the rays; but if this is open, the number of nuclei instantly generated decreases much more slowly than the first power of distance. The fact that to the wooden fog chamber the medium within a sphere of at least 6 meters in radius remains almost equally energized throughout remains a result of importance.

9. *Nucleation Due to Gamma Rays.*— To what extent nucleation is producible by gamma rays may be tested by radium enclosed in a thick chamber of lead. The results are strikingly confirmatory. For instance in case of radium (10,000×) enclosed in a hermetically sealed aluminum tube and placed outside, but close to the end of the fog chamber (bottom nearly 1 cm. thick, walls .3 cm. thick), the data were

Radium in sealed aluminum	$10^{-3}N=$ 27	Transmission	100 per cent.
Radium in lead tube .5 cm. thick	23		85 per cent.
Radium in lead tube 1.0 cm. thick	18		69 per cent.

The nuclei are thus very largely due to this extremely penetrating radiation. By using lead tubes, capped and not capped, 30 cm. and 60 cm. long and placed parallel to the end of fog chamber, no evidence of secondary radiation was discernable, all the effective radiation passing through the lead walls. Hence while the gamma rays of radium contribute but a few percent. of the ionization of the air, they produce nearly the whole of the nucleation.

10. *Distance Effect in Case of Radium.*— In comparison with the abundant nucleation after the penetration specified, the decrease of nucleation observed when the tube is at different distances, D, from the fog chamber is remarkably large. For example

D	= 0	10	30	50	100	200	cm.
$N\times 10^{-3}=$	30	13	8	5	3	2	

If measurement be made from the line of sight (10 cm. from end of fog

[1] Through .14 cm. of lead $10^{-3}N=3$; through .05 cm. of iron $10^{-3}N=44$.

chamber) the nucleation decreases less rapidly than the first power of distance. Hence whereas the distance effect in case of X-rays is small, it is very large in radium. On the other hand, rays from radium show remarkable nucleating power after penetrating many centimeters of lead, whereas the nucleating power of the X-rays after such penetration is relatively negligible.

11. *Axial Nucleation Within the Fog Chamber.*— Finally, when the rays have once entered the fog chamber, the nucleation along the axis seems nearly uniform. Measurements are difficult, but while the nucleation decreases to nearly one-fourth when the radium is placed on the outside of the fog chamber, 40 cm. (axially) from the end, the coronas along 40 cm. within the fog chamber are nearly of the same aperture for any given position of the radium tube.

OPTICAL ROTATION BY A QUARTZ PRISM.[1]

BY H. M. REESE.

IN this paper, which is merely a preliminary note, the author has investigated mathematically the form of the diffraction pattern which would result from a rectangular opening if the beam of light were polarized, not all in the same azimuth, but in an azimuth which varies uniformly from one side of the beam to the other. Such a beam is furnished by a quartz prism cut so that the optic axis is parallel to the base of the prism and normal to its refracting edge if the incident light is plane polarized. The theory indicates two principal maxima instead of one, the general form of the pattern depending upon the width of the beam as compared to the rotating power of the quartz. The phase-relations show that the two principal maxima are circularly polarized in opposite senses. This shows that Fresnel's observation that plane-polarized light is resolved into two circularly polarized components can be explained purely on the basis of diffraction.

POLARIZATION OF STANDARD CELLS.[1]

BY R. R. RAMSEY.

MY purpose in performing the experiments described below was to determine the character of the polarization of cells, containing mercurous sulphate, when they are connected to a battery. The cells

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

were made according to the usual formula for cadmium cells of the H form. Connections were made as in Fig. 1. S is the cell under investigation. E is a battery of five cells. A is milliammeter. C is a commutator. R is a resistance box. PP' is a potentiometer. B is the potentiometer battery. G is a galvanometer in the potentiometer circuit. R' is a resistance box. K is a contact key by means of which any one of six cells (one of which was never used except as a standard) could be

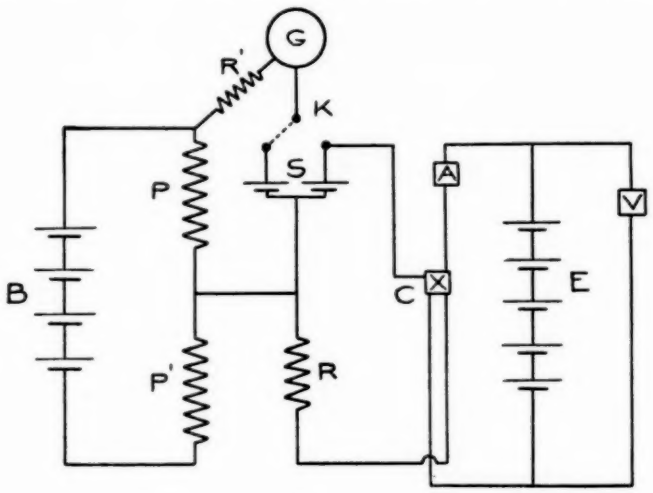


Fig. 1.

thrown into the potentiometer circuit, C being open. By opening K and closing C current could be forced through the cell under investigation in the direct or reversed direction. By varying the resistance, R, the approximate resistance of the cell could be determined. From the current, the resistances in the circuit, and the difference of potential at the terminal of the battery, E, the e.m.f. of the cell, S, could be determined. In the first runs, the change in the potential of the cells is shown by plotting the current as ordinates and time as abscissas. In cells the diameter of whose mercury electrode is 1 cm. with a current of about four milliamperes, the initial current is proportional to the total e.m.f. in the circuit, curve I, Fig. 2. The current gradually decreases and reaches a steady value in about ten minutes. This steady value being proportional to the e.m.f. of the battery E. After remaining constant from two to four hours, say, the current rapidly decreases to an unsteady value near zero. If the current is broken at any time after the first decrease, the potentiometer shows its e.m.f. to be a few hundredths volts. The The e.m.f. gradually increases and after short runs the cell may regain

its original e.m.f. to within a few thousandths of a volt. After very extended runs the cells recover very slowly, in one case from 0.017 to 0.084 volts in two weeks. If the current is reversed after the cell has been run down, the current increases to a maximum in about ten minutes and then rapidly decreases to an unsteady value near zero, Curve 3 and 5, Fig. 2. Potentiometer readings after a run show the e.m.f. to be near

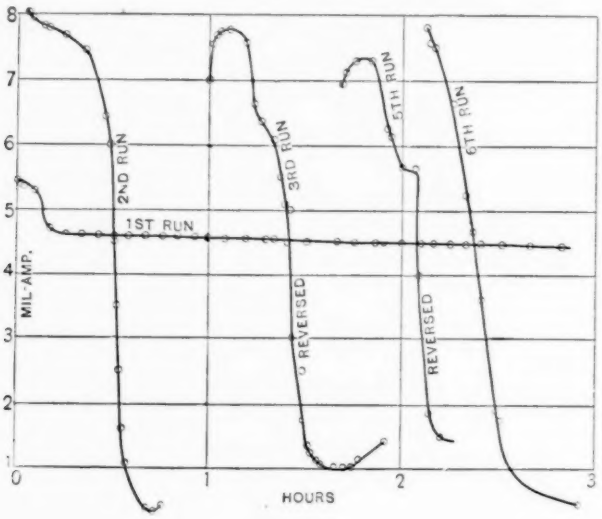


Fig. 2.

the normal value. A double *H* cell was made with three electrodes, two of mercury and one of cadmium. Connections were made with the cadmium and one of the mercury electrodes and the cell allowed to run down. The potentiometer shows the e.m.f. between the cadmium and second electrode to be normal, showing the polarization to be at the mercury terminal.

ON THE MEASUREMENT OF CURRENT BY A QUADRANT ELECTROMETER.[1]

BY O. M. STEWART.

CASE investigated is that where the current flowing into a conductor connected to one pair of quadrants is measured by determining the velocity of the needle. This is the usual method in radioactivity work.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

Two cases are considered: First, that where the change in capacity of the electrometer due to the motion of the needle does not appreciably affect the capacity of the apparatus. And second, the more general case, where the capacity is treated as a variable.

It is shown that after the needle has reached uniform motion the current is proportional to the angular velocity of the needle. A simple method is given for finding the time it requires for the needle to reach this uniform speed. When the capacity is constant the time for the needle to acquire a velocity within say 2 per cent. of the final velocity is the same as the time required for the needle to return when grounded to a vibration having an amplitude of 2 per cent. of the original steady deflection.

In the second case it is shown that after the velocity has become constant, the effective capacity becomes constant and has then the value given by Professor J. J. Thomson.[1] The ratio of the effective capacity to the capacity when the needle does not move can be obtained from the ratio of the deflection when the quadrants are connected to a certain potential to the deflection when the quadrants had only been connected a very short time.

It is found that the maximum sensibility for current work does not coincide with the maximum sensibility for steady deflections. When the potential of the needle is changed until the effective capacity is twice the capacity when at zero and not allowed to move, the electrometer will be the most sensitive. This however is true only when the potential of the needle is below the potential giving maximum sensibility for ordinary deflections. It is worth consideration when the capacity connected to the electrometer is small compared to that of the electrometer itself.

The equations deduced for the motion of the needle show that the deflection reached in a definite time after the ground is broken is in all cases proportional to the current. It is not necessary in this method to wait until the velocity has become uniform. It is however necessary to eliminate the disturbance sometimes caused by the breaking of the ground connection.

Surface Tension by the Method of Liquid Jets.[2]

By Floyd R. Watson.

WHEN a liquid issues horizontally from a small, nearly circular orifice in a thin wall of a vessel, the stream formed assumes a definite shape, the boundaries of which are fixed. In the case of an

[1] Philosophical Magazine.

[2] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

elliptical orifice the shape of the jet may be likened roughly to that of a link chain, the links—crests—being first horizontal, then vertical, giving the appearance of standing waves on the stream. Fig. 1 is a photograph of such a stream.

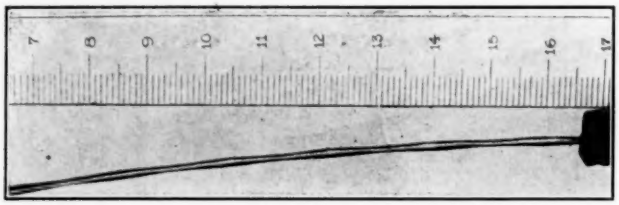


Fig. 1.

The complete explanation of the properties of the jet was given by Rayleigh[1] in 1879. The equation deduced for this case is as follows[2]:

$$p = \pi^{\frac{1}{2}} A^{-\frac{1}{2}} \sqrt{\frac{T}{\rho}} \sqrt{n^3 - n}$$

where $p/2\pi$ is the frequency of the motion; A is the mean cross-section of the jet; T the surface tension; ρ the density; and n the mode of vibration, being equal to unity for a circular jet, two for a jet from an elliptical orifice, three for a jet from a triangular orifice, etc. As the frequency $p/2\pi$ equals the velocity divided by the wave-length v/λ, the equation may be written,

$$\lambda = \frac{2\pi^{\frac{1}{2}} v A^{\frac{1}{2}}}{\sqrt{n^3 - n}} \sqrt{\frac{\rho}{T}}$$

from which the surface tension is expressed as

$$T = \frac{4\pi^{\frac{1}{2}} v^2 A^{\frac{1}{2}}}{(n^3 - n)\lambda^2} \rho.$$

The tension may then be calculated when values are found for λ, v, and A.

The method of measurement used was suggested by Rayleigh[1] though he did not use this formula for the absolute determination of surface tension. The apparatus used is shown in Fig. 2. A glass bulb D which can be raised or lowered, contains the liquid whose tension is to be determined. A rubber tube fastened to the base of this bulb allows the liquid to pass to a horizontal tube B and thence to the air through an elliptical orfice about 1 mm. in diameter. A transparent glass scale C is attached to B in a vertical plane that includes the axis of the jet.

[1] Proc. Roy. Soc., 29, 71, also Theory of Sound, Vol. 2, §§ 357, 358.
[2] Theory of Sound, Vol. 2, § 358, equation 1.
[3] Proc. Roy. Soc., 47, 281.

The velocity v is calculated from the relation $v = \sqrt{2gh}$, h being the vertical distance from the level of the liquid in D to the level of the orifice in B. A is found from the relation $m = vAt\rho$, where m is the mass of fluid that passes through the orifice in the time t. The value of λ is obtained by measuring the distance between two adjacent crests on the jet. This measurement is subject to error in that the wave-lengths are small — from 1½ to 3 cm. — and that it is difficult to estimate the position of the center of each crest. Further, as λ depends on the pressure head h which is constantly decreasing, an element of haste is introduced.

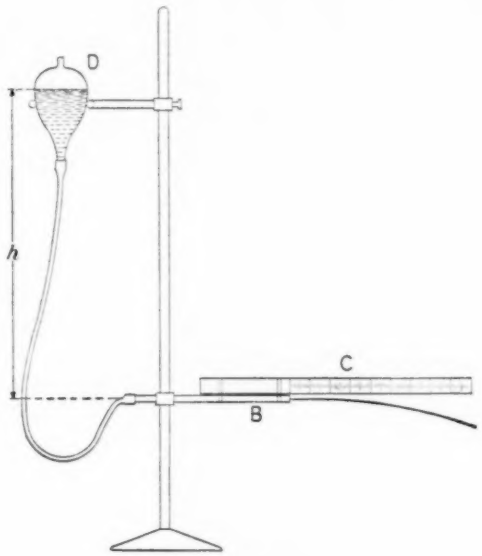


Fig. 2.

Special means were taken to lessen these chances for error. The jet was placed in front of a lecture lantern so that its shadow was thrown on the screen, thus magnifying the distance λ about 20 times. λ was then measured with a beam compass and read off on the scale C which was also thrown on the screen and magnified in the same proportion as the jet. Fig. 1 is copied from a photograph of the screen when the shadow of a jet of water was thrown on it. The time of exposure was about 20 seconds, and the head h diminished about 3 cm.

Measurements were taken by the above method for water, water contaminated with oil, mercury, and mercury wet with water. The following table gives results :

Date.	Liquid.	λ	h	m	t	Temp.	T
Mar. 23	water.	3λ=5.3 cm.	39 cm.	98.8 gms.	20 sec.	21 C	69.1
" 29	water.	3λ=5.53 "	44.6 "	133.1 "	25.2 "	23.5	70.5
" 29	water and oil.	3λ=2.48 "				"	39.8
" 29	water repeated.	3λ=5.46 "	42.0 "	141.2 "	27.2 "	"	71.3
" 27	mercury.	λ=1.5 "	16.1 "	852 "	20 "	22 C	527
" 27	mercury wet with water.	λ=1.5 "	16.5 "			"	527?
April 3	mercury.	2λ=3.44 "	19.0 "	1006 "	21 "	21.1	495
" 3	mercury wet with water.	2λ=3.41 "	18.3 "			"	484.8

The tensions found for water are less than the values found by other methods, the accepted value being about 73 dynes per cm. at 23° C. The effect of oil on water is interesting. Oil was forced into the aperture from which the jet escaped, then a water jet was set up which passed through this layer of oil. The tension dropped from 70.5 dynes to 39.8 dynes; then as the oil became washed out, the jet changed its form back to the water jet and the tension rose to its former value. From this measurement it seems that a newly-formed water surface when contaminated slightly with oil does not drop immediately in tension. This is in accordance with a result found by Rayleigh[1] where a freshly formed surface of soap solution had nearly the same tension as pure water.

The results found for mercury are not so satisfactory as the water tensions; the values varying from 527 to 495 dynes per cm. for different days. Yet both of these values are good ones compared with previous work done by the writer,[2] where the highest tension found was 510 dynes per cm. Good results should be expected by this method for the surfaces are not exposed long enough to the air to cause the tension to drop.

Tensions for mercury wet with water do not show an appreciable variation from the tensions of mercury supposedly not wet. Two conclusions seem probable in this connection; first, that the mercury was wet in *both* measurements, and second, that a fresh surface of wet mercury has nearly the same tension as dry mercury. It is not improbable that the mercury was wet all the time, for the reason that it was cleaned with concentrated H_2SO_4 and pasty mercurous sulphate.[3]

[1] Proc. Roy. Soc., 47, 281.
[2] PHYS. REV., 12, 257.
[3] PHYS. REV., 12, 264.

Comparison of the Mutual Inductance of a Pair of Coils With The Self Inductance of One of Them.[1]

By Robert T. Herdegen.

MAXWELL'S method[2] is modified so as to permit the use of the differential transformer as a measuring instrument.[3] The balance condition being equality of amplitude and phase of the two currents in the differential transformer simplifies the expression for the ratio of L to M. The sharpness of the balance makes it possible to determine this ratio to an accuracy of one-tenth per cent. for a single observation.

The Radius of Molecular Attraction.[1]

By C. W. Chamberlain.

IT has been suggested that it would be impossible for a liquid film to exist, the thickness of part of which is less than twice the radius of molecular attraction. Quinke reached the conclusion that the radius of molecular attraction is approximately equal to $5(10)^{-6}$ cm. Johonott found that the minimum thickness which a soap film can attain is $6(10)^{-7}$ cm., while the limiting thickness attained by the first black is $1.2(10)^{-6}$ cm.

If Johonott's measurement of the limiting thickness of a liquid film can be taken as a determination of the radius of molecular attraction, the discrepancy between this value and that of Quinke remains to be explained.

A silver wedge was formed upon a plate of optical glass and Quinke's method employed for finding the point at which the thickness of the silver was equal to the radius of molecular attraction. Quinke estimated this thickness by its color. An attempt was made to measure the thickness by means of a Michelson interferometer. If Quinke's value $5(10)^{-6}$ cm. is correct, assuming the index of refraction of silver to be .25, the shift in the interferometer ought to be .15 of a fringe. The shifting of the fringe was in every case less than this amount.

A multiple reflection or compound interferometer was devised, suitable for making rapid and accurate measurements of thin wedges of small area. Light incident on a plane parallel plate provided with a thin film of silver was reflected and refracted to two mirrors placed at angles of 67½

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

[2] El. and Mag., Vol. II., p. 365.

[3] A. Trowbridge, Phys. Rev., CVII., February, 1905.

degrees to the plane parallel plate. The light was reflected from these two mirrors in paths parallel to each other to a third mirror and then to a fourth. The third and fourth mirror made a slight angle with each other and the parallel rays were thus reflected many times between them and finally returned along their entering paths where they were made to recombine and interfere. By changing the angle between the third and fourth mirror by means of a single adjusting screw the instrument could be compounded from one to twenty times. It possessed the advantage of showing interference fringes of several powers in the field of view at the same time. The observer could quickly and conveniently select that power best suited to the measurement of the magnitude under investigation.

As it was desirable to test the accuracy of Quinke's determination and as Kundt's value for the index of refraction of silver is somewhat in doubt, the silver wedges were changed into silver iodide before their thickness was measured.

The work has progressed far enough to indicate that Quinke's value for the radius of molecular attraction is at least twice too large.